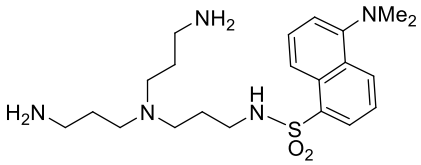
Supporting Information

Macrocyclic compounds comprising tris(3-aminopropyl)amine units and fluorophore moieties: synthesis and spectroscopic studies in the presence of metal salts

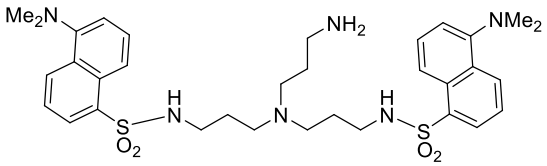
Daria S. Kuliukhina, Nataliya M. Chernichenko, Alexei D. Averin, Anton S. Abel, Olga A. Maloshitskaya and Irina P. Beletskaya

Experimental procedures and spectral data for compounds 2-5, 7-11, 13-16, 18-25.

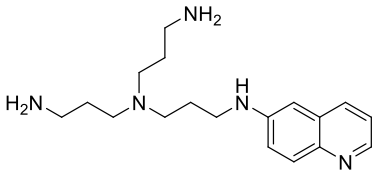
Synthesis



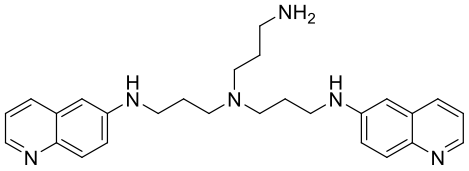
***N*-(3-(bis(3-aminopropyl)amino)propyl)-5-(dimethylamino)naphthalene-1-sulfonamide (2)**. A one-neck flask was charged with tris(3-aminopropyl)amine (**1**) (413 mg, 2.2 mmol), acetonitrile (15 ml) and K_2CO_3 (303 mg, 2.2 mmol). Dansyl chloride (308 mg, 1.1 mmol) was dissolved in acetonitrile (30 ml) and was slowly added during 5 h. The solution was filtered, the residue was washed with dichloromethane, combined organic fractions were evaporated *in vacuo* and the residue was chromatographed on silica gel using a sequence of eluents: CH_2Cl_2, CH_2Cl_2 – MeOH 100:1-3:1, CH_2Cl_2 – MeOH – NH_3aq 100:20:1 – 10:4:1. The target compound **2** was isolated with the eluent CH_2Cl_2 – MeOH – NH_3aq 100:20:5. Yield 239 mg (50%), light-yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.44 (quintet, 4H, ^3J = 7.0 Hz, CCH_2C), 1.47 (quintet, 2H, ^3J = 5.9 Hz, CCH_2C), 2.25-2.28 (m, 6H, CH_2N), 2.59 (t, 4H, ^3J = 6.9 Hz, CH_2N), 2.79 (s, 6H, CH_3), 2.89 (t, 2H, ^3J = 5.9 Hz, CH_2N), 3.17 (br. s, 4H, NH_2), 7.09 (d, 1H, ^3J = 7.6 Hz, H6(Np)), 7.43 (t, 1H, $^3J_{obs}$ = 7.4 Hz, H3 or H7(Np)), 7.46 (t, 1H, $^3J_{obs}$ = 8.1 Hz, H7 or H3(Np)), 8.14 (d, 1H, $^3J_{obs}$ = 7.3 Hz, H2(Np)), 8.30 (d, 1H, ^3J = 8.6 Hz, H8(Np)), 8.43 (d, 1H, ^3J = 8.5 Hz, H4(Np)), NH proton was not unambiguously assigned. ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 25.4 ($C\underline{C}H_2C$), 29.5 ($2C\underline{C}H_2C$), 40.1 ($2CH_2N$), 42.7 (CH_2N), 45.2 ($2CH_3$), 51.3 ($2CH_2N$), 52.6 (CH_2N), 114.8 (C6(Np)), 119.1 (CH(Np)), 123.0 (CH(Np)), 127.8 (CH(Np)), 129.0 (CH(Np)), 129.5 (C(Np)), 129.6 (C(Np)), 129.7 (CH(Np)), 135.2 (C1(Np)), 151.6 (C5(Np)). MALDI-TOF calcd for $C_{21}H_{36}N_5O_2S$ $[M+H]^+$ 422.2590, found 422.2571.



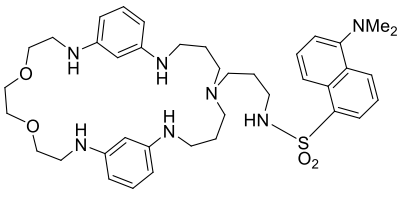
***N*,*N'*-(3,3'-(3-aminopropylazanediyl)bis(propane-3,1-diyl))bis(5-(dimethylamino)-naphtha-lene-1-sulfonamide) (3)**. Isolated as the second product in the synthesis of compound **2**. Eluent CH_2Cl_2 – MeOH – NH_3aq 100:20:1. Yield 92 mg (25%), yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.40 (quintet, 4H, ^3J = 6.3 Hz, CCH_2C), 1.42 (quintet, 2H, ^3J = 6.4 Hz, CCH_2C), 2.12 (t, 4H, ^3J = 6.6 Hz, CH_2N), 2.14 (t, 2H, ^3J = 7.0 Hz, CH_2N), 2.66 (t, 2H, ^3J = 6.5 Hz, CH_2N), 2.81 (t, 4H, ^3J = 7.2 Hz, CH_2N), 2.81 (s, 12H, CH_3), 7.07 (d, 2H, ^3J = 7.6 Hz, H6(Np)), 7.43 (t, 4H, $^3J_{obs}$ = 8.0 Hz, H3, H7(Np)), 8.16 (d, 2H, ^3J = 7.3 Hz, H2(Np)), 8.30 (d, 2H, $^3J_{obs}$ = 8.6 Hz, H8(Np)), 8.45 (d, 2H, ^3J = 8.5 Hz, H4(Np)), NH and NH_2 protons were not unambiguously assigned. ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 25.6 ($2C\underline{C}H_2C$), 27.9 ($C\underline{C}H_2C$), 40.2 (CH_2N), 42.1 ($2CH_2N$), 45.3 ($4CH_3$), 51.6 (CH_2N), 51.7 ($2CH_2N$), 115.0 (2C6(Np)), 119.0 (2CH(Np)), 123.1 (2CH(Np)), 128.1 (2CH(Np)), 129.2 (2CH(Np)), 129.5 (2C(Np)), 129.7 (2C(Np)), 130.0 (2CH(Np)), 135.0 (2C1(Np)), 151.7 (2C5(Np)). MALDI-TOF calcd for $C_{33}H_{47}N_6O_4S_2$ $[M+H]^+$ 655.3100, found 655.3144.



***N*^{1},*N*^{1}-bis(3-aminopropyl)-*N*^{3}-(quinolin-6-yl)propane-1,3-diamine (4)**. A two-neck flask equipped with a magnetic stirrer and reflux condenser flushed with dry argon was charged with 6-bromoquinoline (104 mg, 0.5 mmol), $Pd(dba)_2$ (45 mg, 8 mol%), BINAP (56 mg, 9 mol%). absolute dioxane (10 ml). After stirring for 2 min tris(3-aminopropyl)amine (**1**) (188 mg, 1 mmol) and *t*BuONa (188 mg, 1 mmol) (144 mg, 1.5 mmol) were added, and the reaction mixture was refluxed for 8 h. After the reaction was over the solution was filtered, precipitate was washed with dichloromethane (3x3 ml), combined filtrates were evaporated *in vacuo*, and the residue was chromatographed on silica gel using a sequence of eluents: CH_2Cl_2, CH_2Cl_2 – MeOH 100:1-3:1, CH_2Cl_2 – MeOH – NH_3aq 100:20:1 – 10:4:1. The target compound **4** was isolated with the eluent CH_2Cl_2 – MeOH – NH_3aq 100:20:5. Yield 75 mg (48%), brownish-yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.48 (quintet, 4H, ^{3}J = 7.0 Hz, CCH_2C), 1.66 (quintet, 2H, ^{3}J = 6.7 Hz, CCH_2C), 2.33 (t, 4H, ^{3}J = 7.2 Hz, CH_2N), 2.42 (t, 2H, ^{3}J = 7.1 Hz, CH_2N), 2.55 (t, 4H, ^{3}J = 6.9 Hz, CH_2N), 3.05 (t, 2H, ^{3}J = 6.6 Hz, CH_2NQuin), 6.50 (d, 1H, ^{4}J = 2.3 Hz, H5(Quin)), 6.98 (dd, 1H, ^{3}J = 9.1 Hz, ^{4}J = 2.3 Hz, H7(Quin)), 7.11 (dd, 1H, ^{3}J = 8.2 Hz, ^{3}J = 4.3 Hz, H3(Quin)), 7.61 (d, 1H, ^{3}J = 9.1 Hz, H8(Quin)), 7.79 (d, 1H, ^{3}J = 8.2 Hz, H4(Quin)), 8.30 (d, 1H, ^{3}J = 4.3 Hz, H2(Quin)), NH and NH_2 protons were not unambiguously assigned. ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 25.4 ($C\underline{C}H_2C$), 28.6 ($2C\underline{C}H_2C$), 39.5 ($2CH_2NH_2$), 41.9 (CH_2NQuin), 51.4 ($2CH_2N$), 51.8 (CH_2N), 101.8 (C7(Quin)), 121.0 (CH(Quin)), 121.7 (CH(Quin)), 128.5 (C8(Quin)), 130.2 (C8'(Quin)), 134.1 (C4(Quin)), 141.8 (C4′(Quin)), 144.6 (C2(Quin)), 146.6 (C6(Quin)). MALDI-TOF calcd for $C_{18}H_{30}N_5$ $[M+H]^+$ 316.2501, found 316.2478.

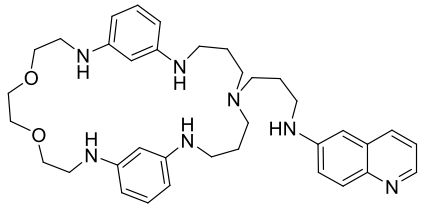


***N*^{1}-(3-aminopropyl)-*N*^{3}-(quinolin-6-yl)-*N*^{1}-(3-(quinolin-6-ylamino)propyl)propane-1,3-diamine (5)**. Isolated as the second product in the synthesis of compound **4**. Eluent CH_2Cl_2 – MeOH – NH_3aq 100:20:2. Yield 27 mg (24%), brownish-yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.63 (quintet, 2H, ^{3}J = 6.9 Hz, CCH_2C), 1.79 (quintet, 4H, ^{3}J = 6.6 Hz, CCH_2C), 2.46 (t, 2H, ^{3}J = 6.7 Hz, CH_2N), 2.53 (t, 4H, ^{3}J = 6.7 Hz, CH_2N), 2.73 (t, 2H, ^{3}J = 6.7 Hz, CH_2N), 3.19 (t, 4H, ^{3}J = 6.4 Hz, CH_2NQuin), 3.40 (br. s, 2H, NH_2), 4.86 (br. s, 2H, NH), 6.57 (d, 2H, ^{4}J = 2.5 Hz, H5(Quin)), 7.02 (dd, 2H, ^{3}J = 9.1 Hz, ^{4}J = 2.5 Hz, H7(Quin)), 7.17 (dd, 2H, ^{3}J = 8.2 Hz, ^{3}J = 4.2 Hz, H3(Quin)), 7.78 (d, 4H, $^{3}J_{obs}$ = 8.7 Hz, H4, H8(Quin)), 8.54 (dd, 2H, ^{3}J = 4.2 Hz, ^{4}J = 1.6 Hz, H2(Quin)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 26.1 ($2C\underline{C}H_2C$), 29.0 ($C\underline{C}H_2C$), 40.3 (CH_2NH_2), 42.7 ($2CH_2$NQuin), 52.3 (CH_2N), 52.5 ($2CH_2N$), 102.4 (2C7(Quin)), 121.3 (2CH(Quin)), 121.4 (2CH(Quin)), 130.0 (2C8(Quin)), 130.2 (2C8′(Quin)), 133.7 (2C4(Quin)), 142.9 (2C4′(Quin)), 145.8 (2C2(Quin)), 146.4 (2C6(Quin)). MALDI-TOF calcd for $C_{27}H_{35}N_6$ $[M+H]^+$ 443.2923, found 443.2956.

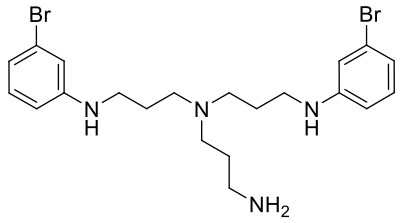


4-(Dimethylamino)-*N*-{3-[19,22-dioxa-2,6,10,16,25-pentaazatricyclo[24.3.1.111,15]-hentriaconta-1(30),11(31),12,14,26,28-hexaen-6-yl]propyl}naphthalene-1-sulfonamide (7) A two-neck flask equipped with a magnetic stirrer and reflux condenser flushed with dry argon was charged with compound **11** (71 mg, 0.1 mmol), $Pd(dba)_2$ (9 mg, 16 mol%), *t*BuDavePhos (6 mg, 20 mol%). absolute dioxane (6 ml). After stirring for 2 min dioxadiamine **12** (22 mg, 0.15 mmol) and *t*BuONa (19 mg, 0.2 mmol) were added, and the reaction mixture was refluxed for 24 h. After the reaction was over the solution was filtered, precipitate was washed with dichloromethane (3x3 ml), combined filtrates were evaporated *in vacuo*, and the residue was chromatographed on silica gel using a sequence of eluents: CH_2Cl_2, CH_2Cl_2 – MeOH 100:1-3:1 The target compound **7** was isolated with the eluent CH_2Cl_2 – MeOH 10:1. Yield 16 mg (23%), brownish-yellow glassy compound. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.68 (br. s, 6H, CCH_2C), 2.52 (br. s, 6H, CH_2N), 2.85 (s, 6H, CH_3), 2.96 (t, 2H, ^{3}J = 6.0 Hz,

CH_2N), 3.05 (t, 4H, ^3J = 6.0 Hz, CH_2NPh), 3.24 (t, 4H, ^3J = 5.0 Hz, CH_2NPh), 3.63 (s, 4H, CH_2O), 3.69 (t, 4H, ^3J = 5.0 Hz, CH_2O), 5.83 (br. s, 2H, H2(Ph)), 5.97 (dd, 2H, ^3J = 8.0 Hz, ^4J = 1.7 Hz, H(Ph)), 6.02 (dd, 2H, ^3J = 8.0 Hz, ^4J = 2.0 Hz, H(Ph)), 6.95 (t, 2H, ^3J = 8.0 Hz, H5(Ph)), 7.12 (d, 1H, ^3J = 7.5 Hz, H6(Np)), 7.45-7.51 (m, 2H, H3, H7(Np)), 8.18 (d, 1H, ^3J = 7.2 Hz, H2(Np)), 8.30 (d, 1H, ^3J = 8.8 Hz, H8(Np)), 8.49 (d, 1H, ^3J = 8.5 Hz, H4(Np)), NH protons were not unambiguously assigned. ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 25.3 (3C$\underline{C}H_2$C), 41.6 ($2CH_2NPh$), 42.2 (CH_2N), 43.6 ($2CH_2NPh$), 45.4 ($2CH_3$), 51.4 ($2CH_2N$), 53.0 (CH_2N), 69.4 ($2CH_2O$), 70.0 ($2CH_2O$), 98.5 (2C2(Ph)), 102.6 (2CH(Ph)), 102.9 (2CH(Ph)), 115.1 (C6(Np)), 119.0 (CH(Np)), 123.2 (CH(Np)), 128.3 (CH(Np)), 129.4 (CH(Np)), 129.6 (C(Np)), 129.8 (C(Np)), 130.1 (2C5(Ph)), 130.2 (CH(Np)), 134.8 (C(Np)), 149.1 (2NC(Ph)), 149.5 (2NC(Ph)), 151.8 (C5(Np)). MALDI-TOF calcd for $C_{39}H_{56}N_7O_4S$ $[M+H]^+$ 718.4114, found 718.3977.

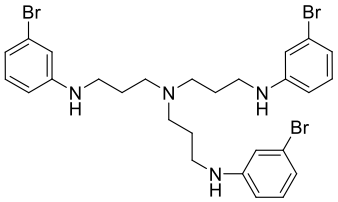


***N*-{3-[19,22-dioxa-2,6,10,16,25-pentaazatricyclo[24.3.1.111,15]hentriaconta-1(30),11(31),12,14,26,28-hexaen-6-yl]propyl}quinoline-6-amine (8)** A two-neck flask equipped with a magnetic stirrer and reflux condenser flushed with dry argon was charged with compound **4** (63 mg, 0.2 mmol), compound **6** (73 mg, 0.16 mmol), $Pd(dba)_2$ (22 mg, 16 mol%), *t*BuDavePhos (15 mg, 20 mol%). absolute dioxane (8 ml). After stirring for 2 min *t*BuONa (69 mg, 0.7 mmol) was added, and the reaction mixture was refluxed for 24 h. After the reaction was over the solution was filtered, precipitate was washed with dichloromethane (3x3 ml), combined filtrates were evaporated *in vacuo*, and the residue was chromatographed on silica gel using a sequence of eluents: CH_2Cl_2, CH_2Cl_2 – MeOH 100:1-3:1 The target compound **8** was isolated with the eluent CH_2Cl_2 – MeOH 10:1. Yield 37 mg (38%), yellow glassy compound. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.75 (quintet, 4H, ^3J = 6.0 Hz, CCH_2C), 1.89 (quintet, 2H, ^3J = 6.5 Hz, CCH_2C), 2.59-2.67 (m, 6H, CH_2N), 3.13 (t, 4H, ^3J = 6.2 Hz, CH_2NPh), 3.21 (t, 4H, ^3J = 5.0 Hz, CH_2NPh), 3.27 (t, 2H, ^3J = 6.7 Hz, CH_2NQuin), 3.60 (s, 4H, CH_2O), 3.65 (t, 4H, ^3J = 5.0 Hz, CH_2O), 5.82 (t, 2H, ^4J = 1.5 Hz, H2(Ph)), 5.97 (dd, 2H, ^3J = 8.0 Hz, ^4J = 1.5 Hz, H(Ph)), 6.02 (dd, 2H, ^3J = 8.0 Hz, ^4J = 1.6 Hz, H(Ph)), 6.61 (d, 1H, ^4J = 2.5 Hz, H5(Quin)), 6.95 (t, 2H, ^3J = 8.0 Hz, H5(Ph)), 7.03 (dd, 1H, ^3J = 9.0 Hz, ^4J = 2.5 Hz, H7(Quin)), 7.22 (dd, 1H, ^3J = 8.3 Hz, ^4J = 4.3 Hz, H3(Quin)), 7.82 (d, 1H, ^3J = 9.0 Hz, H8(Q)), 7.85 (d, 1H, ^3J = 8.3 Hz, H4(Quin)), 8.56 (dd, 1H, ^3J = 4.3 Hz, ^4J = 1.6 Hz, H2(Quin)), NH protons were not unambiguously assigned. ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 26.0 br. (3C$\underline{C}H_2$C), 42.0 ($2CH_2NPh$), 42.2 (CH_2NQuin), 43.5 ($2CH_2NPh$), 50.8 (CH_2N), 52.0 ($2CH_2N$), 69.4 (CH_2O), 70.0 ($2CH_2O$), 98.3 (2CH(Ph)), 102.5 (2CH(Ph), C7(Quin)), 102.9 (2CH(Ph)), 121.3 (CH(Quin)), 121.6 (CH(Quin)), 130.0 (CH(Quin)), 130.1 (2C5(Ph)), 130.2 (C(Quin)), 133.9 (CH(Quin)), 142.9 (C(Quin)), 145.8 (C2(Quin)), 146.3 (NC(Ar)), 149.3 (NC(Ar)), 149.5 (NC(Ar)). MALDI-TOF calcd for $C_{36}H_{50}N_7O_2$ $[M+H]^+$ 612.3988, found , 612.4026.

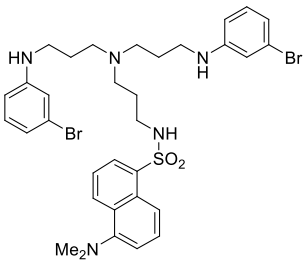


***N*^{1}-(3-aminopropyl)-*N*^{3}-(3-bromophenyl)-*N*^{1}-(3-(3-bromophenylamino)propyl)-propane-1,3-diamine (9)** A two-neck flask equipped with a magnetic stirrer and reflux condenser flushed with dry argon was charged with 1,3-dibromobenzene (472 mg, 2 mmol), $Pd(dba)_2$ (23 mg, 4 мол%), BINAP (28 mg, 4.5 mol%), absolute dioxane (10 ml). After stirring for 2 min tris(3-aminopropyl)amine (**1**) (188 mg, 1 mmol) and *t*BuONa (192 mg, 2 mmol) were added and the reaction mixture was refluxed for 12 h. After the reaction was over the solution was filtered, precipitate was washed with dichloromethane (3x10 ml), combined filtrates were evaporated *in vacuo*, and the residue was chromatographed on silica gel using a sequence of eluents: CH_2Cl_2, CH_2Cl_2 – MeOH 200:1 – 3:1, CH_2Cl_2 – MeOH – NH_3aq 100:20:1 – 100:25:5. The target compound **9** was isolated with the eluent CH_2Cl_2 – MeOH – NH_3aq 100:20:3. Yield 114 mg (23%), yellowish oil. ^{1}H-NMR

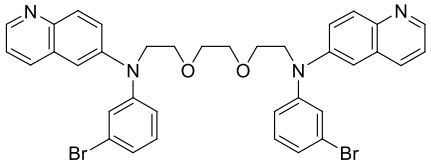
(400 MHz, $CDCl_3$): δ 1.73 (quintet, 6H, ^3J = 6.2 Hz, CCH_2C), 2.51 (t, 6H, ^3J = 6.5 Hz, CH_2N), 2.92 (br. s, 2H, CH_2N), 3.06 (t, 4H, ^3J = 6.4 Hz, CH_2NPh), 4.79 (br. s, 2H, NH), 6.49 (d, 2H, ^3J = 8.0 Hz, H6(Ph)), 6.72 (br. s, 2H, H2(Ph)), 6.74 (d, 2H, ^3J = 7.8 Hz, H4(Ph)), 6.96 (t, 2H, ^3J = 8.0 Hz, H5(Ph)), NH_2 protons were not unambiguously assigned. ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 26.2 (3 $C\underline{C}H_2C$), 40.6 (CH_2NH_2), 42.0 ($2CH_2NPh$), 51.9 ($2CH_2N$), 53.3 (CH_2N), 111.4 (2CH(Ph)), 115.0 (2CH(Ph)), 119.6 (2CH(Ph)), 123.2 (2C3(Ph)), 130.5 (2C5(Ph)), 149.8 (2C1(Ph)). MALDI-TOF calcd for $C_{21}H_{31}Br_2N_4$ $[M+H]^+$ 497.0915, found, 497.0941.



***N*^{1}-(3-bromophenyl)-*N*^{3},*N*^{3}-bis(3-(3-bromophenylamino)propyl)propane-1,3-diamine (10)** Isolated as the second product in the synthesis of compound **9**. Eluent CH_2Cl_2 – MeOH 50:1. Yield 84 mg (19%), yellowish oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.76 (quintet, 6H, ^3J = 6.6 Hz, CCH_2C), 2.53 (t, 6H, ^3J = 6.7 Hz, CH_2N), 3.12 (t, 6H, ^3J = 6.5 Hz, CH_2NPh), 4.23 (br. s, 3H, NH), 6.49 (ddd, 3H, ^3J = 8.2 Hz, ^4J = 2.3 Hz, ^4J = 0.8 Hz, H6(Ph)), 6.72 (t, 3H, ^4J = 2.2 Hz, H2(Ph)), 6.82 (ddd, 3H, ^3J = 7.8 Hz, ^4J = 1.8 Hz, ^4J = 0.8 Hz, H4(Ph)), 7.01 (t, 3H, ^3J = 8.0 Hz, H5(Ph)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 26.2 ($3C\underline{C}H_2C$), 42.2 ($3CH_2NPh$), 52.1 ($3CH_2N$), 111.3 (3CH(Ph)), 114.8 (3CH(Ph)), 119.6 (3CH(Ph)), 123.1 (3C3(Ph)), 130.4 (3C5(Ph)), 149.5 (3C1(Ph)). MALDI-TOF calcd for $C_{27}H_{34}Br_3N_4$ $[M+H]^+$ 651.0334, found, 651.0309.

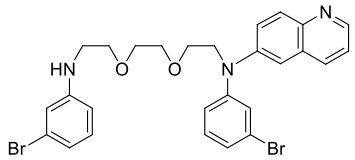


(*N*-(3-(bis(3-(3-bromophenylamino)propyl)amino)propyl)-5-(dimthylamino)naphthalene-1-sulfonamide (11) A one-neck flask was charged with compound **9** (100 mg, 0.2 mmol), 20 ml acetonitrile, dansyl chloride (57 mg 0.20 mmol), potassium carbonate (52 mg, 0.4 mmol), and the reaction mixture was stirred at ambient temperature for 8 h. The solution was filtered, residue was washed with dichloromethane (10 ml), combined organic fractions were evaporated *in vacuo,* and the residue was chromatographed on silica gel using a sequence of eluents: CH_2Cl_2, CH_2Cl_2 – MeOH 200:1 – 3:1. The target compound **11** was isolated with the eluent CH_2Cl_2 – MeOH 20:1. Yield 98 mg (67%), dark-yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.64 (quintet, 2H, ^3J = 6.1 Hz, CCH_2C), 1.70 (quintet, 4H, ^3J = 6.5 Hz, CCH_2C), 2.50 (br. s, 6H, CH_2N), 2.86 (s, 6H, CH_3), 3.00 (t, 2H, ^3J = 5.9 Hz, CH_2N), 3.04 (t, 4H, ^3J = 6.6 Hz, CH_2NPh), 4.12 (br. s, 2H, NH), 6.45 (dd, 2H, ^3J = 8.2 Hz, ^4J = 2.1 Hz, H6(Ph)), 6.67 (t, 2H, ^4J = 1.9 Hz, H2(Ph)), 6.77 (d, 2H, ^3J = 7.8 Hz, H4(Ph)), 6.96 (t, 2H, ^3J = 8.0 Hz, H5(Ph)), 7.12 (d, 1H, ^3J = 7.6 Hz, H6(Np)), 7.46-7.50 (m, 2H, H3, H7(Np)), 8.21 (d, 1H, ^3J = 7.2 Hz, H2(Np)), 8.31 (d, 1H, ^3J = 8.5 Hz, H8(Np)), 8.51 (d, 1H, ^3J = 8.5 Hz, H4(Np)), NH protons were not unambiguously assigned. ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 25.4 ($C\underline{C}H_2C$), 25.8 ($2C\underline{C}H_2C$), 41.8 ($2CH_2NPh$), 42.8 ($2CH_2N$), 51.7 ($2CH_2N$), 53.0 (CH_2N), 111.5 (2CH(Ph)), 114.9 (C6(Np)), 115.0 (2CH(Ph)), 118.8 (CH(Np)), 119.8 (2CH(Ph)), 123.2 (2C3(Ph), CH(Np)), 128.3 (CH(Np)), 129.5 (CH(Np)), 129.6 (C(Np)), 129.8 (C(Np)), 130.4 (CH(Np)), 130.5 (2C5(Ph)), 134.7 (C(Np)), 149.5 (2C1(Ph)), 152.0 (C5(Np)). MALDI-TOF calcd for $C_{33}H_{42}Br_2N_5O_2S$ $[M+H]^+$ 730.1426, found, 730.1385.

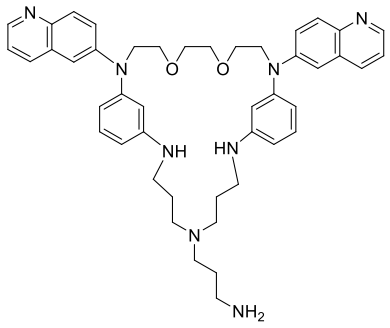


***N,N'*-(2,2'-(ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl))bis(*N*-(3-bromophenyl)quinoline-6-amine) (13)** A two-neck flask equipped with a magnetic stirrer and reflux condenser flushed with dry argon was charged with compound **7** (229 mg, 0.5 mmol), $Pd(dba)_2$ (23 mg, 8 mol%), BINAP (56 mg, 9 mol%), 6-bromoquinoline (312 mg, 1.5 mmol), and dioxane (5 ml). After stirring for 2 min *t*BuONa (96 mg, 1 mmol) was added the reaction was refluxed for 24 h. After the reaction was over the solution was filtered, precipitate was washed with dichloromethane (3x5 ml), combined filtrates were evaporated *in vacuo,* and the residue was chromatographed on

silica gel using a sequence of eluents: CH_2Cl_2, CH_2Cl_2 – MeOH 200:1 – 3:1. The target compound **13** was isolated with the eluent CH_2Cl_2 – MeOH 20:1. Yield 121 mg (34%), dark-yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.55 (s, 4H, CH_2O), 3.68 (t, 4H, ^3J = 5.9 Hz, CH_2O), 3.97 (t, 4H, ^3J = 5.9 Hz, CH_2N), 6.93-6.97 (m, 2H, H6(Ph)), 7.05-7.08 (m, 4H, H2,H5(Ph)), 7.23-7.25 (m, 2H, H4(Ph)), 7.27 (dd, 2H, ^3J = 8.2 Hz, ^3J = 4.2 Hz, H3(Quin)), 7.31 (d, 2H, ^4J = 2.5 Hz, H5(Quin)), 7.39 (dd, 2H, ^3J = 9.2 Hz, ^4J = 2.5 Hz, H7(Quin)), 7.91 (dd, 2H, ^3J = 8.2 Hz, ^4J = 1.6 Hz, H4(Quin)), 8.29 (d, 2H, ^3J = 9.2 Hz, H8(Quin)), 8.73 (dd, 2H, ^3J = 4.2 Hz, ^4J = 1.6 Hz, H2(Quin)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 52.0 ($2CH_2N$), 68.1 ($2CH_2O$), 70.8 ($2CH_2O$), 115.7 (2C7(Quin)), 119.7 (2CH(Ar)), 121.4 (2CH(Ar)), 123.0 (2C3(Ph)), 124.0 (2CH(Ar)), 124.7 (2CH(Ar)), 125.7 (2CH(Ar)), 129.3 (2C(Ar)), 130.3 (2CH(Ar)), 130.5 (2CH(Ar)), 134.7 (2CH(Quin)), 144.7 (2C(Ar)), 144.9 (2C(Ar)), 148.4 (2C2(Quin)), 148.8 (2C(Ar)). MALDI-TOF calcd for $C_{36}H_{33}Br_2N_4O_2$ $[M+H]^+$ 711.0970, found, 711.0949.

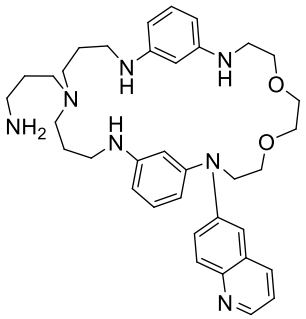


***N*-(3-bromophenyl)-N-(2-(2-(2-(3-bromophenylamino)ethoxy)ethoxy)ethyl)quinolin-6-amine (14)** Obtained as the second product in the synthesis of compound 13 using 1 mmol of compound **7** and 3 mmol of 6-bromoquinoline. Eluent CH_2Cl_2 – MeOH 200:1. Yield 108 mg (18%). dark-yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.20 (t, 2H, ^3J = 5.2 Hz, C<u>H</u>$_2$NH), 3.60 (s, 4H, CH_2O), 3.63 (t, 2H, ^3J = 5.2 Hz, CH_2O), 3.73 (t, 2H, ^3J = 5.8 Hz, CH_2O), 4.04 (t, 2H, ^3J = 5.8 Hz, CH_2N), 4.14 (br. s, 1H, NH), 6.44 (dd, 1H, ^3J = 8.2 Hz, ^4J = 2.3 Hz, H6(Ph)), 6.69 (t, 1H, ^4J = 2.3 Hz, H2(Ph)), 6.78 (dd, 1H, ^3J = 7.9 Hz, ^4J = 2.3 Hz, H4(Ph)), 6.96 (t, 1H, ^3J = 8.0 Hz, H5(Ph)), 7.00-7.04 (m, 1H, H(Ph')), 7.10-7.16 (m, 2H, H(Ar)), 7.28-7.35 (m, 3H, H(Ar)), 7.46 (dd, 1H, ^3J = 9.2 Hz, ^4J = 2.5 Hz, H7(Quin)), 7.99 (d, 1H, ^3J = 7.9 Hz, H4(Quin)), 8.00 (d, 1H, ^3J = 9.2 Hz, H8(Quin)), 8.74 (dd, 1H, ^3J = 4.3 Hz, ^4J = 1.5 Hz, H2(Quin)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 43.2 (CH_2NH), 52.1 (CH_2N), 68.1 (CH_2O), 69.4 (CH_2O), 70.3 (CH_2O), 70.7 (CH_2O), 111.7 (CH(Ph)), 115.3 (2CH(Ar)), 120.1 (2CH(Ar)), 121.4 (CH(Ar)), 123.1 (CBr), 123.2 (CBr), 124.4 (CH(Ar)), 125.1 (CH(Ar)), 125.9 (CH(Ar)), 129.4 (C(Ar)), 129.9 (CH(Ar)), 130.4 (CH(Ar)), 130.6 (CH(Ar)), 135.3 (C4(Quin)), 144.0 (C(Ar)), 145.2 (C(Ar)), 147.8 (C2(Quin)), 148.7 (C(Ar)), 149.4 (C(Ar)). MALDI-TOF calcd for $C_{27}H_{28}Br_2N_3O_2$ $[M+H]^+$ 584.0548, found 584.0571.

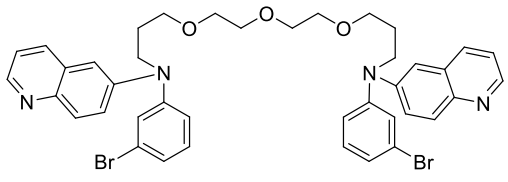


3-[16,25-Diquinolin-6-yl-19,22-dioxa-2,6,10,16,25-pentaazatricyclo[24.3.1.1^{11,15}]-hentriaconta-1(30),11(31),12,14,26,28-hexaen-6-yl]propane-1-amine (15) A two-neck flask equipped with a magnetic stirrer and reflux condenser flushed with dry argon was charged with compound **13** (100 mg, 0.13 mmol), $Pd(dba)_2$ (18 mg, 16 mol%), *t*DavePhos (12 mg, 20 mol%), and dioxane (7 ml). After stirring for 2 min tris(3-aminopropyl)amine (37 mg, 0.2 mmol) and *t*BuONa (37 mg, 0.4 mmol) were added and the reaction was refluxed for 24 h. After the reaction was over the solution was filtered, precipitate was washed with dichloromethane (3x3 ml), combined filtrates were evaporated *in vacuo*, and the residue was chromatographed on silica gel using a sequence of eluents: CH_2Cl_2, CH_2Cl_2 – MeOH 100:1 – 3:1, CH_2Cl_2 – MeOH – NH_3aq 100:20:1 – 100:25:5. The target compound **15** was isolated with the eluent CH_2Cl_2 – MeOH – NH_3aq 100:20:3. Yield 19 mg (19%), brown glassy compound. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.59 (quintet, 2H, ^3J = 7.0 Hz, CCH_2C), 1.70 (quintet, 4H, ^3J = 6.1 Hz, CCH_2C), 2.43 (t, 2H, ^3J = 7.1 Hz, CH_2N), 2.47 (t, 4H, ^3J = 6.5 Hz, CH_2N), 2.69 (t, 2H, ^3J = 6.9 Hz, CH_2N), 3.11 (t, 4H, ^3J = 6.3 Hz, CH_2NPh), 3.54 (s, 4H, CH_2O), 3.68 (t, 4H, ^3J = 5.9 Hz, CH_2O), 3.93 (t, 4H, ^3J = 5.9 Hz, CH_2NQuin), 6.30 (d, 2H, ^3J = 8.5 Hz, H(Ph)), 6.39-6.42 (m, 4H, H(Ph)), 7.04 (t, 2H, ^3J = 8.3 Hz, H5(Ph)), 7.09 (d, 2H, ^4J = 2.7 Hz, H5(Quin)), 7.21 (dd, 2H, ^3J = 8.3 Hz, ^3J = 4.2 Hz, H3(Quin)), 7.32 (dd, 2H, ^3J = 9.3 Hz, ^4J = 2.7 Hz, H7(Quin)), 7.80 (d, 2H, ^3J = 9.3 Hz, H8(Quin)), 7.87 (d, 2H, ^3J = 8.3 Hz,

H4(Quin)), 8.63 (dd, 2H, ^3J = 4.2 Hz, ^4J = 1.2 Hz, H2(Quin)), NH and NH_2 protons were not unambiguously assigned. ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 26.5 (2C$\underline{C}H_2$C), 30.4 (C$\underline{C}H_2$C), 40.4 (CH_2N), 42.8 (2CH_2NPh), 51.9 (2CH_2NQ), 52.1 (CH_2N), 52.6 (2CH_2N), 68.1 (CH_2O), 70.8 (CH_2O), 108.0 (2CH(Ar)), 109.1 (2CH(Ar)), 110.4 (2CH(Ar)), 113.1 (2CH(Ar)), 121.2 (2CH(Ar)), 124.1 (2CH(Ar)), 129.6 (2CH(Ar)), 130.1 (2CH(Ar)), 134.3 (2CH(Ar)), 143.7 (2C(Ar)), 146.1 (2C(Ar)), 146.2 (2C(Ar)), 147.2 (2C2(Quin)), 148.0 (2C(Ar)), 149.8 (2C(Ar)). MALDI-TOF calcd for $C_{45}H_{55}N_8O_2$ $[M+H]^+$ 739.4448, found 739.4492.

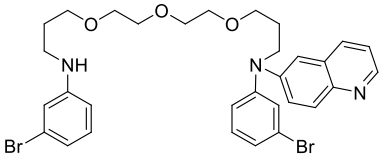


6-(3-Aminopropyl)-16-quinolin-6-yl-19,22-dioxa-2,6,16,25-tetraazatricyclo[24.3.1.111,15]-hentriaconta-1(30),11(31),12,14,26,28-hexaen-10-amine (16) A two-neck flask equipped with a magnetic stirrer and reflux condenser, flushed with dry argon, was charged with compound **14** (108 mg, 0.18 mmol), $Pd(dba)_2$ (23 mg, 16 mol%), DavePhos (15 mg, 18 mol%) and absolute dioxane (8 ml). After stirring for 2 min amine **1** (51 mg, 0.25 mmol) and *t*BuONa (48 mg, 0.5 mmol) were added and the reaction mixture was refluxed for 24 h. After the reaction was over the residue was filtered, washed with dichloromethane (3x3 ml), combined filtrates were evaporated *in vacuo*, and the residue was chromatographed on silica gel using a sequence of eluents: CH_2Cl_2, CH_2Cl_2 – MeOH 100:1 – 3:1, CH_2Cl_2 – MeOH – NH_3aq 100:20:1 – 100:20:3. Target compound **16** was obtained with CH_2Cl_2 – MeOH – NH_3aq 100:20:1 eluent. Yield 33 mg (28%), yellow glassy compound. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.66-1.72 (m, 6H, CCH_2C), 2.45-2.49 (m, 6H, CH_2N), 2.82 (t, 2H, ^3J = 6.5 Hz, C$\underline{H}_2$$NH_2$), 3.07 (t, 2H, ^3J = 6.5 Hz, C$\underline{H}_2$NH), 3.10 (t, 2H, ^3J = 6.4 Hz, C$\underline{H}_2$NH), 3.17 (t, 2H, ^3J = 5.2 Hz, C$\underline{H}_2$NH), 3.59 (s, 4H, CH_2O), 3.60 (t, 2H, ^3J = 5.2 Hz, CH_2O), 3.74 (t, 2H, ^3J = 5.8 Hz, CH_2O), 3.87 (br. s, 5H, NH, NH_2), 4.01 (t, 2H, ^3J = 5.8 Hz, CH_2N), 5.78 (t, 1H, ^4J = 1.6 Hz, H(Ph)), 5.87 (dd, 1H, ^3J = 7.9 Hz, ^4J = 1.6 Hz, H(Ph)), 5.97 (dd, 1H, ^3J = 8.0 Hz, ^4J = 1.6 Hz, H(Ph)), 6.35 (dd, 1H, ^3J = 8.1 Hz, ^4J = 2.0 Hz, H(Ph')), 6.44 (t, 1H, ^4J = 2.0 Hz, H(Ph')), 6.52 (dd, 1H, ^3J = 7.8 Hz, ^4J = 2.0 Hz, H(Ph')), 6.90 (t, 1H, ^3J = 8.0 Hz, H(Ph)), 7.10 (t, 1H, ^3J = 8.0 Hz, H(Ph')), 7.17 (d, 1H, ^4J = 2.6 Hz, H5(Quin)), 7.25 (dd, 1H, 8.3 Hz, ^3J = 4.3 Hz, H3(Quin)), 7.40 (dd, 1H, ^3J = 9.2 Hz, ^4J = 2.6 Hz, H7(Quin)), 7.84 (d, 1H, ^3J = 9.2 Hz, H8(Quin)), 7.91 (dd, ^3J = 8.3 Hz, ^4J = 1.7 Hz, H4(Quin)), 8.65 (dd, 1H, ^3J = 4.3 Hz, ^4J = 1.7 Hz, H2(Quin)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 26.2 (C$\underline{C}H_2$C), 26.5 (C$\underline{C}H_2$C), 28.0 (C$\underline{C}H_2$C), 40.4 (CH_2NH_2), 42.4 (CH_2NH), 42.5 (CH_2NH), 43.6 (CH_2NH), 52.0 (2CH_2N), 52.1 (CH_2N), 52.9 (CH_2N), 68.2 (CH_2O), 69.6 (CH_2O), 70.3 (CH_2O), 70.8 (CH_2O), 98.1 (CH(Ph)), 102.3 (CH(Ph)), 103.3 (CH(Ph)), 108.0 (CH(Ph')), 108.7 (CH(Ph')), 111.1 (CH(Ph')), 112.7 (CH(Ar)), 121.2 (CH(Ar)), 124.5 (CH(Ar)), 129.5 (CH(Ar), C(Quin)), 129.9 (CH(Ar)), 130.2 (CH(Ar)), 134.4 (C4(Ar)), 143.7 (C(Ar)), 146.2 (C(Ar)), 147.2 (C2(Quin)), 148.1 (C(Ar)), 149.3 (2C(Ar)), 149.8 (C(Ar)). MALDI-TOF calcd for $C_{36}H_{50}N_7O_2$ $[M+H]^+$ 612.4026, found 612.3967.

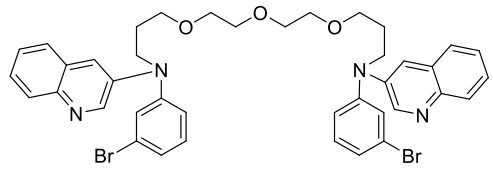


***N,N'*-(3,3'-(2,2'-oxybis(ethane-2,1-diyl)bis(oxy))bis(propane-3,1-diyl))bis(*N*-(3-bromophenyl)quinolin-6-amine) (18)** A two-neck flask equipped with a magnetic stirrer and reflux condenser, flushed with dry argon, was charged with compound **17** (530 mg, 1 mmol), 6-bromoquinoline (624 mg, 3 mmol), $Pd(dba)_2$ (92 mg, 16 mol%), BINAP (112 mg, 18 mol%) and absolute dioxane (10 ml). After stirring for 2 min *t*BuONa (240 mg, 2.5 mmol) was added and the reaction mixture was refluxed for 15 h. After the reaction was over the residue was filtered, washed with dichloromethane (3x3 ml), combined filtrates were evaporated *in vacuo*, and the residue was chromatographed on silica gel using a sequence of eluents: CH_2Cl_2, CH_2Cl_2 – MeOH 500:1 – 5:1. Target compound **18** was obtained with CH_2Cl_2 – MeOH 500:1 eluent. Yield 111 mg (14%), yellow glassy compound. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.92 (quintet, 4H, ^3J =

6.3 Hz, CCH_2C), 3.52 (t, 4H, ^3J = 5.8 Hz, CH_2O), 3.58-3.62 (m, 4H, CH_2O), 3.69-3.73 (m, 4H, CH_2O), 3.93 (t, 4H, ^3J = 6.9 Hz, CH_2N), 6.97-7.01 (m, 2H, H(Ph)), 7.08-7.165 (m, 4H, H(Ph)), 7.22 (br. s, 2H, H2(Ph)), 7.30 (d, 2H, ^4J = 2.7 Hz, H5(Quin)), 7.32 (dd, 2H, ^3J = 8.2 Hz, ^3J = 4.2 Hz, H3(Quin)), 7.43 (dd, 2H, ^3J = 9.1 Hz, ^4J = 2.7 Hz, H7(Quin)), 7.97 (d, 2H, ^3J = 9.1 Hz, H8(Quin)), 8.00 (d, 2H, ^3J = 8.2 Hz, H4(Quin)), 8.73 (dd, 2H, ^3J = 4.2 Hz, ^4J = 1.5 Hz, H2(Quin)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 27.5 (2C$\underline{C}H_2$C), 49.1 ($2CH_2N$), 68.0 ($2CH_2O$), 70.3 ($2CH_2O$), 70.7 ($2CH_2O$), 115.2 (2CH(Ar)), 120.0 (2CH(Ar)), 121.4 (2CH(Ar)), 123.1 (2CBr), 124.1 (2CH(Ar)), 124.9 (2CH(Ar)), 126.0 (2CH(Ar)), 129.5 (2C(Quin)), 129.9 (2CH(Ar)), 130.6 (2CH(Ar)), 135.2 (2C4(Quin)), 144.0 (2C(Ar)), 145.3 (2C(Ar)), 147.8 (2C2(Quin)), 148.9 (2C(Ar)). MALDI-TOF calcd for $C_{40}H_{41}Br_2N_4O_3$ $[M+H]^+$ 783.1545, found 783.1593.

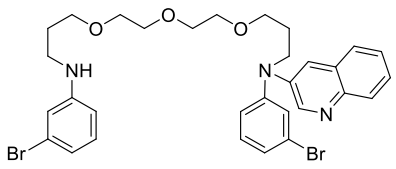


***N*-(3-bromophenyl)-N-(3-(2-(2-(3-(3-bromophenylamino)propoxy)ethoxy)ethoxy)propyl)-quinolin-6-amine (19)** Obtained as the second product in the synthesis of compound **18**. CH_2Cl_2 – MeOH 100:1 eluent. Yield 122 mg (19%), yellow glassy compound. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.83 (quintet, 2H, ^3J =6.0 Hz, CCH_2C), 1.94 (quintet, 2H, ^3J = 6.4 Hz, CCH_2C), 3.16 (t, 2H, ^3J = 6.4 Hz, C$\underline{H}_2$NH), 3.52 (t, 2H, ^3J = 5.8 Hz, CH_2O), 3.56 (t, 2H, ^3J = 5.8 Hz, CH_2O), 3.58-3.62 (m, 4H, CH_2O), 3.66-3.70 (m, 4H, CH_2O), 3.94 (t, 2H, ^3J = 6.9 Hz, CH_2N), 4.26 (br. s, 1H, NH), 6.46 (ddd, 1H, ^3J = 8.2 Hz, ^4J = 2.2 Hz, ^4J = 0.8 Hz, H6(Ph)), 6.69 (t, 1H, ^4J = 2.0 Hz, H2(Ph)), 6.73 (ddd, 1H, ^3J = 7.8 Hz, ^4J = 1.7 Hz, ^4J = 0.8 Hz, H4(Ph)), 6.94 (t, 1H, ^3J = 8.0 Hz, H5(Ph)), 6.99 (1H, dt, ^3J = 7.1 Hz, ^4J = 2.2 Hz, H(Ph')), 7.06-7.14 (m, 2H, H(Ph')), 7.23 (br. s, 1H, H2(Ph')), 7.29-7.33 (m, 2H, H3, H5(Quin)), 7.45 (dd, 1H, ^3J = 9.2 Hz, ^4J = 2.6 Hz, H7(Quin)), 7.97 (d, 1H, ^3J = 9.2 Hz, H8(Quin)), 7.99 (d, 1H, ^3J = 8.5 Hz, H4(Quin)), 8.74 (dd, 1H, ^3J = 4.2 Hz, ^4J = 1.6 Hz, H2(Quin)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 27.4 (C$\underline{C}H_2$C), 28.7 (C$\underline{C}H_2$C), 41.6 (CH_2NH), 49.1 (CH_2N), 68.0 (CH_2O), 69.7 (CH_2O), 70.1 (CH_2O), 70.2 (CH_2O), 70.5 ($2CH_2O$), 111.2 (CH(Ph)), 114.9 (CH(Ph)), 115.3 (CH(Ph)), 119.3 (CH(Ar)), 119.8 (CH(Ar)), 121.3 (CH(Ar)), 123.0 (CBr), 123.1 (CBr), 123.9 (CH(Ar)), 124.6 (CH(Ar)), 125.9 (CH(Ar)), 129.4 (C(Quin)), 130.0 (CH(Ar)), 130.3 (CH(Ar)), 130.5 (CH(Ar)), 134.0 (C4(Quin)), 144.2 (C(Ar)), 145.2 (C(Ar)), 148.0 (C2(Quin)), 148.9 (C(Ar)), 149.8 (C(Ar)). MALDI-TOF calcd for $C_{40}H_{41}Br_2N_4O_3$ $[M+H]^+$ 656.1123, found 656.1155.

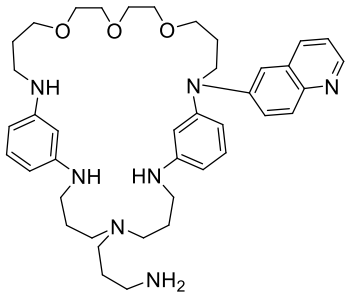


***N,N'*-(3,3'-(2,2'-oxybis(ethane-2,1-diyl)bis(oxy))bis(propane-3,1-diyl))bis(N-(3-bromophenyl)quinolin-3-amine) (20)** A two-neck flask equipped with a magnetic stirrer and reflux condenser, flushed with dry argon, was charged with compound **17** (530 mg, 1 mmol), 3-bromoquinoline (416 mg, 2 mmol), $Pd(dba)_2$ (92 mg, 16 mol%), BINAP (112 mg, 18 mol%) and absolute dioxane (10 ml). After stirring for 2 min *t*BuONa (192 mg, 2 mmol) was added and the reaction mixture was refluxed for 15 h. After the reaction was over the residue was filtered, washed with dichloromethane (3x3 ml), combined filtrates were evaporated *in vacuo*, and the residue was chromatographed on silica gel using a sequence of eluents: CH_2Cl_2, CH_2Cl_2 – MeOH 200:1 – 5:1. Target compound **20** was obtained with CH_2Cl_2 – MeOH 50:1 eluent. Yield 143 mg (18%), yellow glassy compound. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.92 (quintet, 4H, ^3J = 5.8 Hz, CCH_2C), 3.51 (t, 4H, ^3J = 5.7 Hz, CH_2O), 3.58-3.62 (m, 4H, CH_2O), 3.69-3.73 (m, 4H, CH_2O), 3.92 (t, 4H, ^3J = 6.9 Hz, CH_2N), 6.94 (dt, 2H, $^3J_{obs}$ = 6.9 Hz, $^4J_{obs}$ = 2.4 Hz, H(Ph)), 7.04-7.12 (m, 4H, H(Ph)), 7.20 (br. s, 2H, H2(Ph)), 7.44-7.49 (m, 2H, H7(Quin)), 7.55 (ddd, 2H, ^3J = 8.4 Hz, ^3J = 7.0 Hz, ^4J = 1.5 Hz, H6(Quin)), 7.66-7.70 (m, 4H, H4, H8(Quin)), 8.01 (d, 2H, ^3J = 9.0 Hz, H5(Quin)), 8.68 (d, 2H, ^4J = 2.7 Hz, H2(Quin)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 27.3 (2C$\underline{C}H_2$C), 49.0 ($2CH_2N$), 67.8 ($2CH_2O$), 70.3 ($2CH_2O$), 70.6 ($2CH_2O$), 118.8 (2CH(Ar)), 123.0 (2CH(Ar)), 123.2 (2CBr), 123.8 (2CH(Ar)), 124.5 (2CH(Ar)), 126.7 (2CH(Ar)), 127.0 (2CH(Ar)), 127.4 (2CH(Ar)), 128.7 (2C(Ar)), 128.9 (2CH(Ar)), 130.6

(2CH(Ar)), 140.4 (2C(Ar)), 147.8 (2C2(Quin)), 148.6 (2C(Ar)), 149.4 (2C(Ar)). MALDI-TOF calcd for $C_{40}H_{41}Br_2N_4O_3$ $[M+H]^+$ 783.1545, found 783.1496.

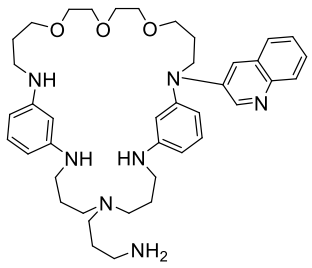


***N*-(3-bromophenyl)-N-(3-(2-(2-(3-(3-bromophenylamino)propoxy)ethoxy)ethoxy)propyl)-quinolin-3-amine (21)** Obtained as the second product in the synthesis of compound **20**. CH_2Cl_2 – MeOH 100:1 eluent. Yield 189 mg (29%), yellow glassy compound. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.84 (quintet, 2H, ^3J = 6.1 Hz, CCH_2C), 1.95 (quintet, 2H, ^3J = 6.3 Hz, CCH_2C), 3.17 (t, 2H, ^3J = 6.3 Hz, $C\underline{H}_2NH$), 3.54 (t, 2H, ^3J = 5.7 Hz, CH_2O), 3.57 (t, 2H, ^3J = 5.6 Hz, CH_2O), 3.58-3.63 (m, 4H, CH_2O), 3.67-3.72 (m, 4H, CH_2O), 3.95 (t, 2H, ^3J = 7.0 Hz, CH_2N), 4.29 (br. s, 1H, NH), 6.47 (ddd, 1H, ^3J = 8.2 Hz, ^4J = 2.3 Hz, ^4J = 0.8 Hz, H6(Ph)), 6.70 (t, 1H, ^3J = 2.1 Hz, H2(Ph)), 6.74 (ddd, 1H, ^3J = 7.8 Hz, ^4J = 1.8 Hz, ^4J = 0.8 Hz, H4(Ph)), 6.95-6.98 (m, 1H, H(Ph')), 6.96 (t, 1H, ^3J = 8.0 Hz, H5(Ph)), 7.07-7.14 (m, 2H, H(Ph')), 7.20-7.22 (m, 1H, H2(Ph')), 7.49 (ddd, 1H, ^3J = 8.1 Hz, ^3J = 7.0 Hz, ^4J = 1.2 Hz, H7(Quin)), 7.57 (ddd, 1H, ^3J = 8.4 Hz, ^3J = 7.0 Hz, ^4J = 1.5 Hz, H6(Quin)), 7.67-7.70 (m, 2H, H4, H8(Quin)), 8.02 (d, 1H, ^3J = 8.4 Hz, H5(Quin)), 8.70 (d, 1H, ^4J = 2.7 Hz, H2(Quin)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 27.3 ($C\underline{C}H_2C$), 28.7 ($C\underline{C}H_2C$), 41.7 (CH_2NH), 49.0 (CH_2N), 67.9 (CH_2O), 69.7 (CH_2O), 70.2 (CH_2O), 70.3 (CH_2O), 70.6 ($2CH_2O$), 111.3 (CH(Ph)), 115.0 (CH(Ph)), 118.8 (CH(Ar)), 119.4 (CH(Ar)), 123.0 (CH(Ar)), 123.1 (CBr), 123.2 (CBr), 123.8 (CH(Ar)), 124.6 (CH(Ar)), 126.8 (CH(Ar)), 127.0 (CH(Ar)), 127.4 (CH(Ar)), 128.8 (C(Ar)), 128.9 (CH(Ar)), 130.3 (CH(Ar)), 130.6 (CH(Ar)), 140.5 (C(Ar)), 143.9 (C(Ar)), 147.9 (C2(Quin)), 148.7 (C(Ar)), 149.8 (C(Ar)). MALDI-TOF calcd for $C_{40}H_{41}Br_2N_4O_3$ $[M+H]^+$ 656.1123, found 656.1149.

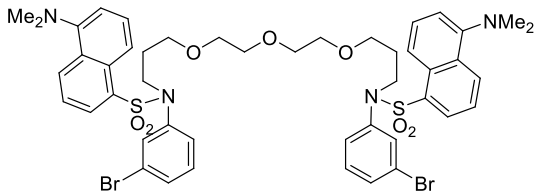


6-(3-Aminopropyl)-16-quinolin-6-yl-20,23,26-trioxa-2,6,16,30-tetraazatricyclo-[29.3.1.111,15]hexa-triaconta-1(35),11(36),12,14,31,33-hexaen-10-amine (22) A two-neck flask equipped with a magnetic stirrer and reflux condenser, flushed with dry argon, was charged with compound **19** (122 mg, 0.186 mmol), $Pd(dba)_2$ (26 mg, 16 mol%), DavePhos (20 mg, 18 mol%) and absolute dioxane (8 ml). After stirring for 2 min amine **1** (53 mg, 0.28 mmol) and *t*BuONa (54 mg, 0.56 mmol) were added and the reaction mixture was refluxed for 24 h. After the reaction was over the residue was filtered, washed with dichloromethane (3x3 ml), combined filtrates were evaporated *in vacuo*, and the residue was chromatographed on silica gel using a sequence of eluents: CH_2Cl_2, CH_2Cl_2 – MeOH 100:1 – 3:1, CH_2Cl_2 – MeOH – NH_3aq 100:20:1 – 100:20:3. Target compound **22** was obtained with CH_2Cl_2 – MeOH – NH_3aq 100:20:2 eluent. Yield 21 mg (17%), yellow glassy compound. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.60 (quintet, 2H, ^3J = 7.0 Hz, CCH_2C), 1.67-1.76 (m, 4H, CCH_2C), 1.80 (quintet, 2H, ^3J = 6.1 Hz, CCH_2C), 1.95 (quintet, 2H, ^3J = 6.4 Hz, CCH_2C), 2.43-2.51 (m, 6H, CH_2N), 2.70 (t, 2H, ^3J = 6.9 Hz, $C\underline{H}_2NH_2$), 3.08-3.16 (m, 6H, $C\underline{H}_2NH$), 3.52 (t, 2H, ^3J = 6.0 Hz, CH_2O), 3.53-3.60 (m, 6H, CH_2O), 3.64-3.69 (m, 4H, CH_2O), 3.89 (t, 2H, ^3J = 7.0 Hz, CH_2N), 5.79 (br. s, 1H, H(Ph)), 5.90-5.95 (m, 2H, H(Ph)), 6.30-6.36 (m, 2H, H(Ph')), 6.48 (dd, 1H, ^3J = 8.0 Hz, ^4J = 1.4 Hz, H(Ph')), 6.89 (t, 1H, ^3J = 8.0 Hz, H5(Ph)), 7.11 (t, 1H, ^3J = 7.9 Hz, H5(Ph')), 7.12 (d, 1H, ^4J = 2.6 Hz, H5(Quin)), 7.26 (dd, 1H, ^3J = 8.2 Hz, ^3J = 4.3 Hz, H3(Quin)), 7.37 (dd, 1H, ^3J = 9.3 Hz, ^4J = 2.6 Hz, H7(Quin)), 7.83 (d, 1H, ^3J = 9.3 Hz, H8(Quin)), 7.93 (d, 1H, ^3J = 8.2 Hz, H4(Quin)), 8.65 (dd, 1H, ^3J = 4.3 Hz, ^4J = 1.4 Hz, H2(Quin)), NH and NH_2 protons were not unambiguously assigned. ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 26.4 ($C\underline{C}H_2C$), 26.7 ($C\underline{C}H_2C$), 27.6 ($C\underline{C}H_2C$), 29.2 ($C\underline{C}H_2C$), 30.3 ($C\underline{C}H_2C$), 40.4 (CH_2NH_2), 41.6 (CH_2NH), 42.7 (CH_2NH), 43.0 (CH_2NH), 49.1 (CH_2N), 52.0 (CH_2N), 52.6 (CH_2N), 52.8 (CH_2N), 68.5 (CH_2O), 69.3 (CH_2O), 70.2 ($2CH_2O$), 70.7 ($2CH_2O$), 97.2 (CH(Ph)), 102.2 (CH(Ph)), 102.4 (CH(Ph)), 107.8 (CH(Ph')), 108.7 (CH(Ph')), 110.7 (CH(Ph')), 112.9 (CH(Quin)), 121.1 (CH(Quin)), 124.4 (CH(Quin)), 129.5 (CH(Ar)), 129.6 (C(Quin)), 129.8 (CH(Ar)), 130.2 (CH(Ar)), 134.3 (C4(Quin)), 143.7

(C(Ar)), 146.2 (C(Ar)), 147.1 (C2(Quin)), 148.4 (C(Ar)), 149.5 (C(Ar)), 149.7 (C(Ar)), 149.9 (C(Ar)). MALDI-TOF calcd for $C_{40}H_{58}N_7O_3$ $[M+H]^+$ 684.4601, found 684.4630.

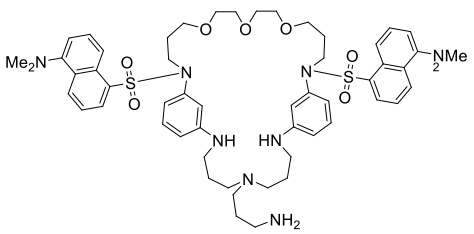


6-(3-Aminopropyl)-16-quinolin-3-yl-20,23,26-trioxa-2,6,16,30-tetraazatricyclo-[29.3.1.111,15]hexatriaconta-1(35),11(36),12,14,31,33-hexaen-10-amine (23) A two-neck flask equipped with a magnetic stirrer and reflux condenser, flushed with dry argon, was charged with compound **21** (129 mg, 0.19 mmol), $Pd(dba)_2$ (26 mg, 16 mol%), *t*BuDavePhos (18 mg, 20 mol%) and absolute dioxane (8 ml). After stirring for 2 min amine **1** (54 mg, 0.285 mmol) and *t*BuONa (55 mg, 0.57 mmol) were added and the reaction mixture was refluxed for 24 h. After the reaction was over the residue was filtered, washed with dichloromethane (3x3 ml), combined filtrates were evaporated *in vacuo*, and the residue was chromatographed on silica gel using a sequence of eluents: CH_2Cl_2, CH_2Cl_2 – MeOH 100:1 – 3:1, CH_2Cl_2 – MeOH – NH_3aq 100:20:1 – 100:20:3. Target compound **23** was obtained with CH_2Cl_2 – MeOH – NH_3aq 100:20:1 eluent. Yield 37 mg (28%), yellow glassy compound. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.60 (quintet, 2H, ^3J = 7.1 Hz, CCH_2C), 1.67-1.76 (m, 4H, CCH_2C), 1.80 (quintet, 2H, ^3J = 6.0 Hz, CCH_2C), 1.93 (quintet, 2H, ^3J = 6.4 Hz, CCH_2C), 2.42-2.51 (m, 6H, CH_2N), 2.70 (t, 2H, ^3J = 6.9 Hz, $C\underline{H}_2NH_2$), 3.10 (t, 2H, ^3J = 6.6 Hz, $C\underline{H}_2NH_2$), 3.14 (t, 2H, ^3J = 6.5 Hz, $C\underline{H}_2NH_2$), 3.52 (t, 2H, ^3J = 5.7 Hz, CH_2O), 3.56 (t, 2H, ^3J = 5.7 Hz, CH_2O), 3.57-3.62 (m, 4H, CH_2O), 3.65-3.69 (m, 4H, CH_2O), 3.89 (t, 2H, ^3J = 7.0 Hz, CH_2N), 5.80 (t, 1H, ^4J = 2.0 Hz, H(Ph)), 5.90-5.95 (m, 2H, H(Ph)), 6.28-6.32 (m, 2H, H(Ph')), 6.45 (dd, 1H, ^3J = 8.4 Hz, H(Ph')), 6.89 (t, 1H, ^3J = 7.9 Hz, H5(Ph)), 7.10 (t, 1H, ^3J = 8.3 Hz, H5(Ph')), 7.41-7.49 (m, 3H, H4, H6, H7(Quin)), 7.64 (dd, 1H, ^3J = 7.6 Hz, ^4J = 1.8 Hz, H8(Quin)), 7.95 (dd, 1H, ^3J = 8.0 Hz, ^4J = 1.3 Hz, H5(Quin)), 8.66 (d, 1H, ^4J = 2.7 Hz, H2(Quin)), NH and NH_2 protons were not unambiguously assigned. ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 26.4 ($C\underline{C}H_2C$), 26.8 ($C\underline{C}H_2C$), 27.4 ($C\underline{C}H_2C$), 29.2 ($C\underline{C}H_2C$), 30.6 ($C\underline{C}H_2C$), 40.5 (CH_2NH_2), 41.6 (CH_2NH), 42.8 (CH_2NH), 43.1 (CH_2NH), 48.9 (CH_2N), 52.0 (CH_2N), 52.6 (CH_2N), 52.9 (CH_2N), 68.3 (CH_2O), 69.6 (CH_2O), 70.3 ($2CH_2O$), 70.7 ($2CH_2O$), 97.2 (CH(Ph)), 102.2 (CH(Ph)), 102.4 (CH(Ph)), 107.5 (2CH(Ph')), 111.7 (CH(Ph')), 119.1 (CH(Quin)), 126.1 (CH(Quin)), 126.4(CH(Quin)), 126.7 (CH(Quin)), 128.7 (CH(Quin)), 129.1 (C(Quin)), 129.8 (CH(Ar)), 129.8 (CH(Ar)), 130.3 (CH(Ar)), 141.6 (C(Ar)), 142.7 (C(Ar)), 146.8 (C2(Quin)), 148.0 (C(Ar)), 149.6 (C(Ar)), 149.7 (C(Ar)), 150.0 (C(Ar)). MALDI-TOF calcd for $C_{40}H_{58}N_7O_3$ $[M+H]^+$ 684.4601, found 684.4573.



***N,N'*-(3,3'-(2,2'-oxybis(ethane-2,1-diyl)bis(oxy))bis(propane-3,1-diyl))bis(*N*-(3-bromophenyl)-5-(dimethylamino)naphthalene-1-sulfonamide) (24)** A one-neck flask equipped with a magnetic stirrer was charged with compound **17** (265 mg, 0.5 mmol), solubilized in 1 ml dichloromethane, acetonitrile (7 ml), dansyl chloride (337 mg, 1.25 mmol), K_2CO_3 (345 mg, 2.5 mmol) were added, and the reaction mixture was stirred for 12 h at room temperature. The residue was filtered, washed with dichloromethane (3x5 ml), combined organic fractions were evaporated *in vacuo*, the residue was chromatographed on silica gel using a sequence of eluents: CH_2Cl_2, CH_2Cl_2 – MeOH 200:1 – 50:1. Target compound **24** was obtained with CH_2Cl_2 – MeOH –200:1 eluent. Yield 351 mg (70%), yellow glassy compound. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.68 (quintet, 4H, ^3J = 6.5 Hz, CCH_2C), 2.86 (s, 12H, CH_3N), 3.40 (t, 4H, ^3J = 6.1 Hz, CH_2O), 3.40-3.43 (m, 4H, CH_2O), 3.48-3.52 (m, 4H, CH_2O), 3.67 (t, 4H, ^3J = 6.9 Hz, CH_2N), 7.03 (d, 2H, ^3J = 8.1 Hz, H6(Ph)), 7.08 (t, 2H, ^3J = 7.9 Hz, H5(Ph)), 7.13 (d, 2H, ^3J =7.5 Hz, H6(Np)), 7.17 (t, 2H, ^4J = 1.8 Hz, H2(Ph)), 7.34 (d, 2H, ^3J = 7.8 Hz, H4(Ph)), 7.39 (t, 2H, ^3J = 8.1 Hz, H3 or H7(Np)), 7.43 (t, 2H, ^3J = 7.9 Hz, H7 or H3(Np)), 8.05 (d, 2H, ^3J = 8.7 Hz, H8(Np)), 8.08 (d, 2H, ^3J = 7.2 Hz, H2(Np)), 8.53 d, 2H, ^3J = 8.4 Hz, H4(Np)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 28.5 ($2C\underline{C}H_cC$), 45.3 ($4CH_3N$), 47.7 ($2CH_2N$), 67.7 ($2CH_2O$), 70.0 ($2CH_2O$), 70.3 ($2CH_2O$),

115.1 (2CH(Ar)), 119.6 (2CH(Ar)), 122.0 (2CBr), 123.0 (2CH(Ar)), 127.7 (2CH(Ar)), 127.8 (2CH(Ar)), 129.6 (4C((Np)), 130.0 (2CH(Ar)), 130.6 (2CH(Ar)), 130.7 (2CH(Ar)), 130.9 (2CH(Ar)), 131.9 (2CH(Ar)), 133.5 (2C1(Np)), 140.3 (2C1(Ph)), 151.3 (2C5(Np)). MALDI-TOF calcd for $C_{46}H_{53}Br_2N_4O_7S_2$ $[M+H]^+$ 995.1722, found 995.1775.



(5-{[6-(3-aminopropyl)-30-{[5-(dimethylamino)-1-naphthyl]sulfonyl}-20,23,26-trioxa-2,6,10,16,30-pentaazatricyclo[29.3.1.111,15]hexatriaconta-1(35),11(36),12,14,31,33-hexaen-16-yl]sulfonyl}-1-naphthyl)dimethylamine (25) A two-neck flask equipped with a magnetic stirrer and reflux condenser, flushed with dry argon, was charged with compound **24** (351 mg, 0.35 mmol), $Pd(dba)_2$ (46 mg, 8 mol%), *t*BuDavePhos (31 mg, 9 mol%) and absolute dioxane (18 ml). After stirring for 2 min amine **1** (99 mg, 0.5 mmol) and *t*BuONa (96 mg, 1 mmol) were added and the reaction mixture was refluxed for 24 h. After the reaction was over the residue was filtered, washed with dichloromethane (3x3 ml), combined filtrates were evaporated *in vacuo*, and the residue was chromatographed on silica gel using a sequence of eluents: CH_2Cl_2, CH_2Cl_2 – MeOH 200:1 – 3:1. Target compound **25** was obtained with CH_2Cl_2 – MeOH 3:1 eluent. Yield 92 mg (26%), yellow glassy compound. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.69 (quintet, 8H, ^3J = 6.4 Hz, CCH_2C), 1.80 (quintet, 2H, ^3J = 6.5 Hz, CCH_2C), 2.48-2.55 (m, 6H, CH_2N), 2.84 (s, 12H, CH_3N), 2.96-3.02 (m, 6H, $C\underline{H}_2NH$), 3.32-3.36 (m, 4H, CH_2O), 3.36 (t, 4H, ^3J = 6.6 Hz, CH_2O), 3.44-3.44 (m, 4H, CH_2O), 3.61 (t, 4H, ^3J = 6.8 Hz, CH_2N), 4.92 (br. s, 2H, NH), 6.18 (dd, 2H, ^3J = 7.7 Hz, ^4J = 1.0 Hz, H(Ph)), 6.44 (dd, 2H, ^3J = 8.1 Hz, ^4J = 1.7 Hz (H(Ph)), 6.48 (br. s, 2H, H2(Ph)), 6.87 (t, 2H, ^3J = 7.9 Hz, H5(Ph)), 7.10 (d, 2H, ^3J = 7.3 Hz, H6(Np)), 7.39 (t, 2H, $^3J_{obs}$ = 7.8 Hz, H3 or H7(Np)), 7.41 (t, 2H, $^3J_{obs}$ = 7.5 Hz, H7 or H3(Np)), 8.09 (dd, 2H, ^3J = 7.3 Hz, ^4J = 1.2 Hz, H2(Np)), 8.13 (d, 2H, ^3J = 8.7 Hz, H8(Np)), 8.47 (d, 2H, ^3J = 8.5 Hz, H4(Np)), NH_2 protons were not unambiguously assigned. ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 25.6 ($2C\underline{C}H_2C$), 28.5 ($3C\underline{C}H_2C$), 40.4 (CH_2NH_2), 42.0 ($2CH_2NH$), 45.4 ($4CH_3N$), 47.7 ($2CH_2N$), 51.6 ($2CH_2N$), 53.0 (CH_2N), 68.2 ($2CH_2O$), 69.9 ($2CH_2O$), 70.3 ($2CH_2O$), 112.1 (2CH(Ph)), 113.9 (2CH(Ph)), 115.0 (2C6(Np)), 116.5 (2CH(Ph)), 120.1 (2CH(Np)), 123.1 (2CH(Np)), 127.1 (2CH(Np)), 129.4 (2CH(Np)), 129.7 (2C(Np)), 130.2 (2C(Np)), 130.3 (2CH(Ar)), 130.8 (2CH(Ar)), 134.3 (2C1(Np)), 139.5 (2C(Ph)), 149.0 (2C(Ph)), 151.4 (2c5(Np)). MALDI-TOF calcd for $C_{55}H_{75}N_8O_7S_2$ $[M+H]^+$ 1023.5200, found 1023.50.

Spectroscopic investigations

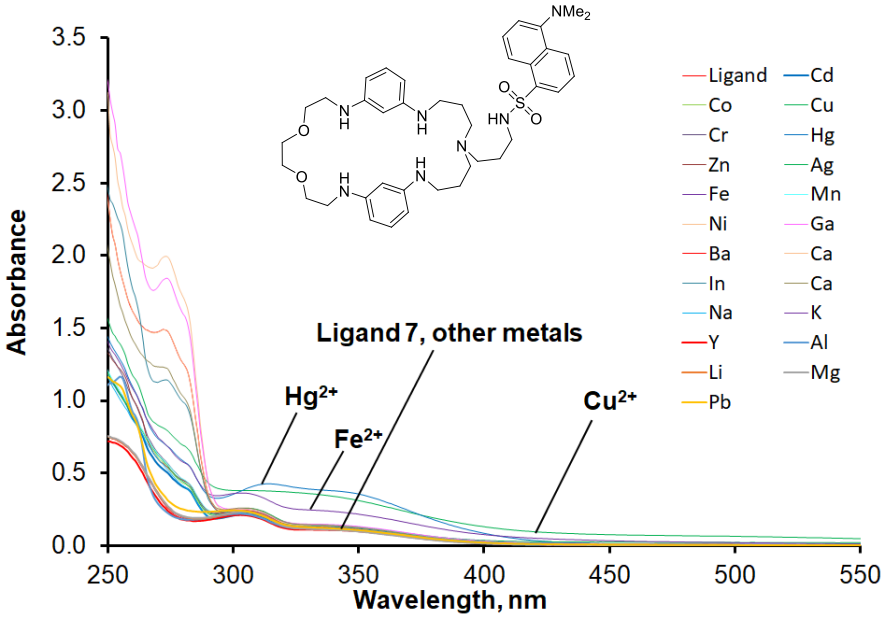


Figure S1. UV-vis spectra of compound **7** in acetonitrile in the presence of Li(I), Na(I), K(I), Mg(II), Ca(II), Ba(II), Al(III), Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Pb(II), Ag(I), Ga(III), In(III), Y(III) (5 equiv.). C_L 4.8 μM.

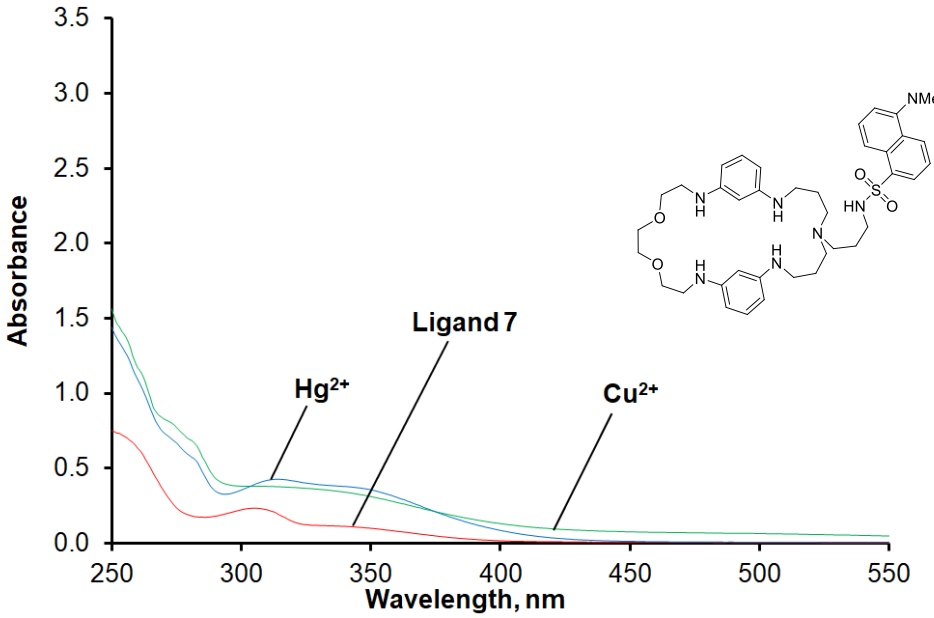


Figure S2. UV-vis spectra of compound **7** in acetonitrile in the presence of selected metal cations: Cu(II) and Hg(II) (5 equiv.). C_L 4.8*μM.

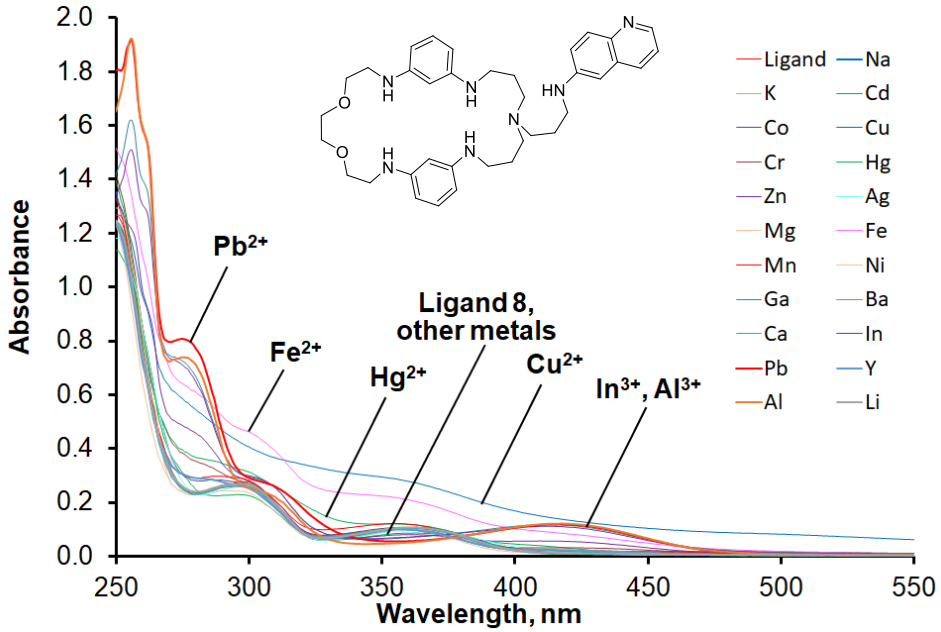


Figure S3. UV-vis spectra of compound **8** in acetonitrile in the presence of Li(I), Na(I), K(I), Mg(II), Ca(II), Ba(II), Al(III), Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Pb(II), Ag(I), Ga(III), In(III), Y(III) (5 equiv.). C_L 23.0 μM.

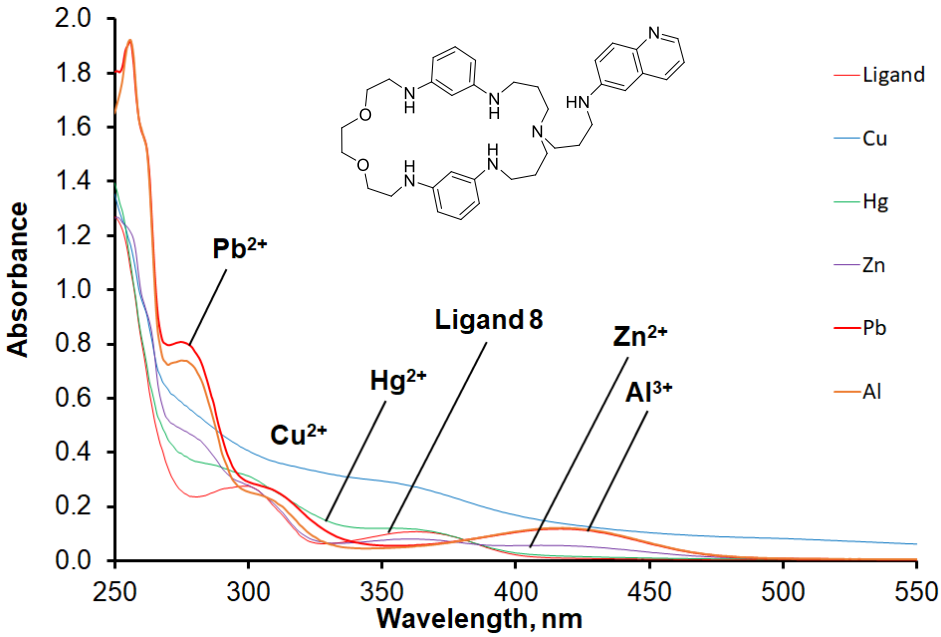


Figure S4. UV-vis spectra of compound **8** in acetonitrile in the presence of selected metal cations: Cu(II), Hg(II), Zn(II), Pb(II), Al(III) (5 equiv.). C_L 23.0 μM.

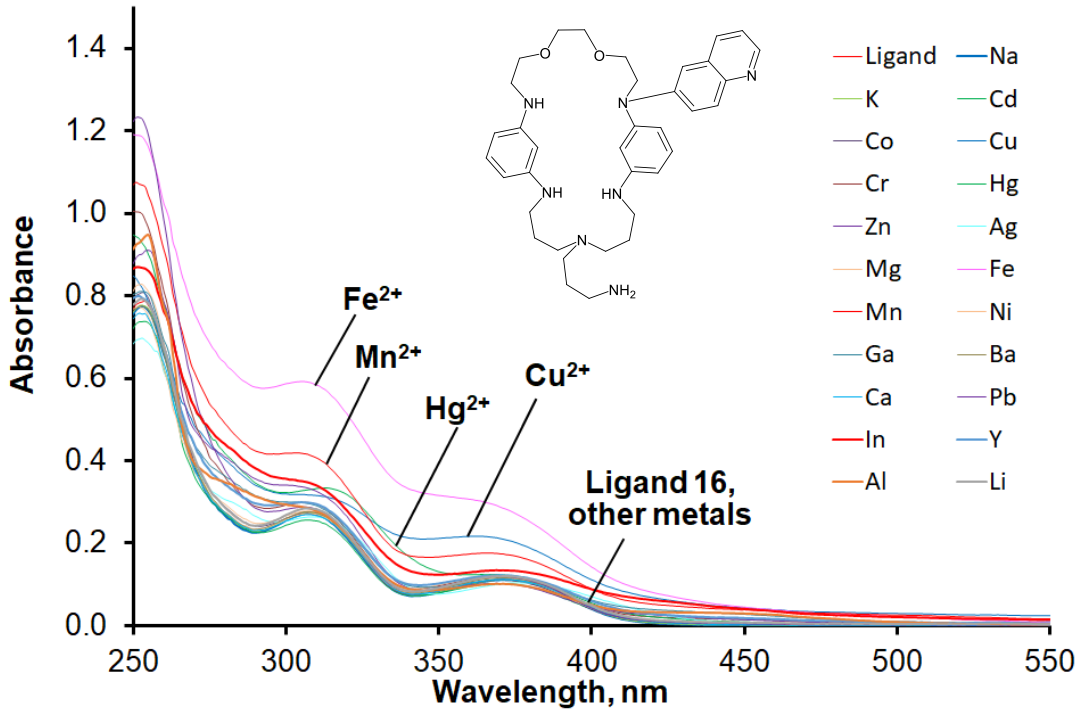


Figure S5. UV-vis spectra of compound **16** in acetonitrile in the presence of Li(I), Na(I), K(I), Mg(II), Ca(II), Ba(II), Al(III), Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Pb(II), Ag(I), Ga(III), In(III), Y(III) (5 equiv.). C_L 17.5 μM.

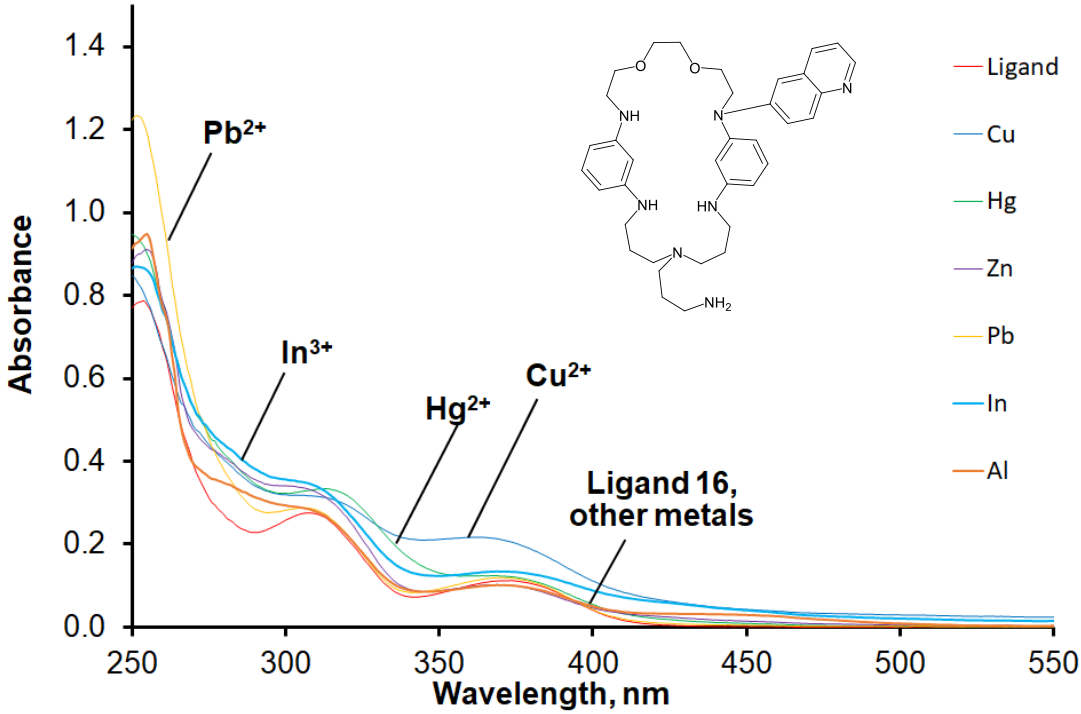


Figure S6. UV-vis spectra of compound **16** in acetonitrile in the presence of selected metal cations: Cu(II), Hg(II), Zn(II), Pb(II), Al(III), In(III) (5 equiv.). C_L 17.5 μM.

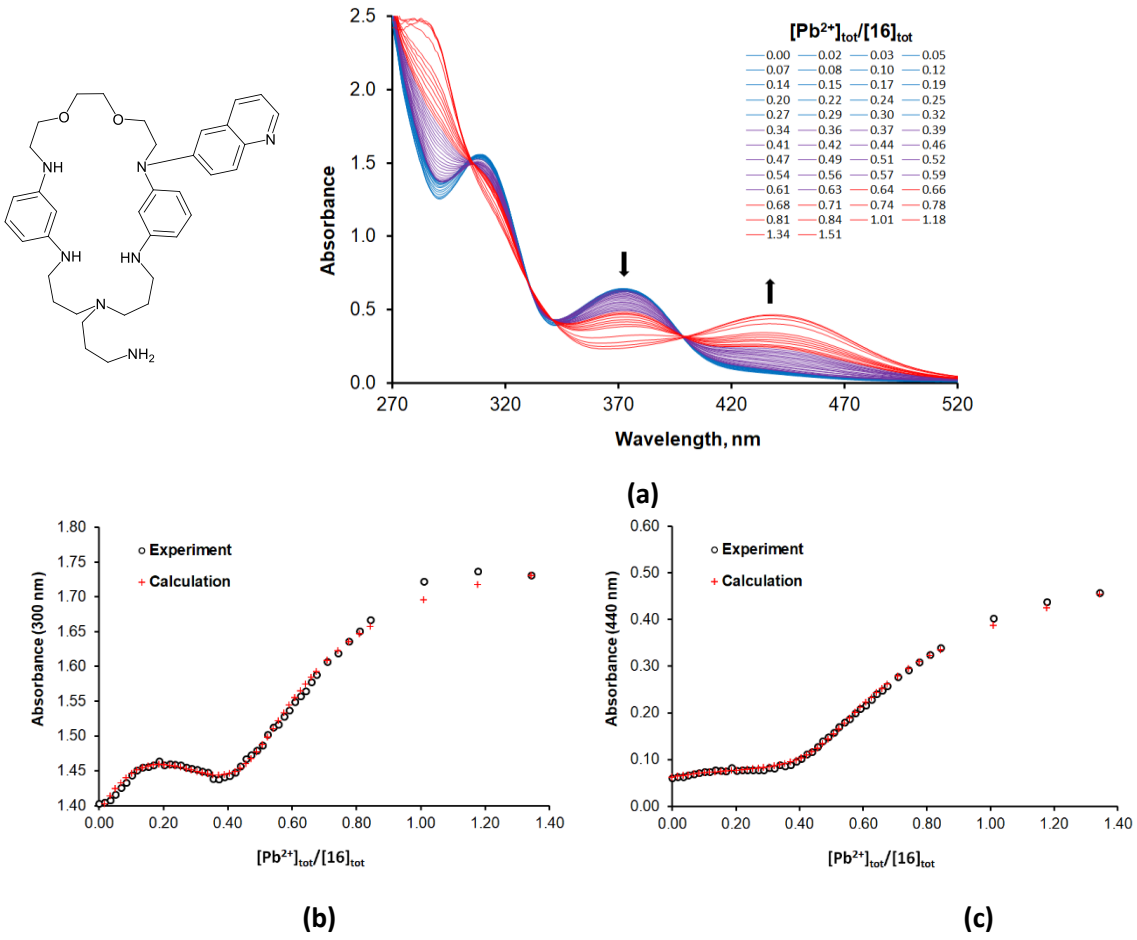


Figure S7. (a) Evolution of the UV–vis absorption spectrum of **16** ($[\mathbf{16}]_{tot}$ = 318 μM, MeCN) upon addition of $Pb(ClO_4)_2$ (0–1.5 equiv.). (b) Changes of the absorbance as a function of the $[Pb^{2+}]_{tot}/[\mathbf{16}]_{tot}$ ratio at λ =300 nm. (c) Changes of the absorbance as a function of the $[Pb^{2+}]_{tot}/[\mathbf{16}]_{tot}$ ratio at λ =440 nm.

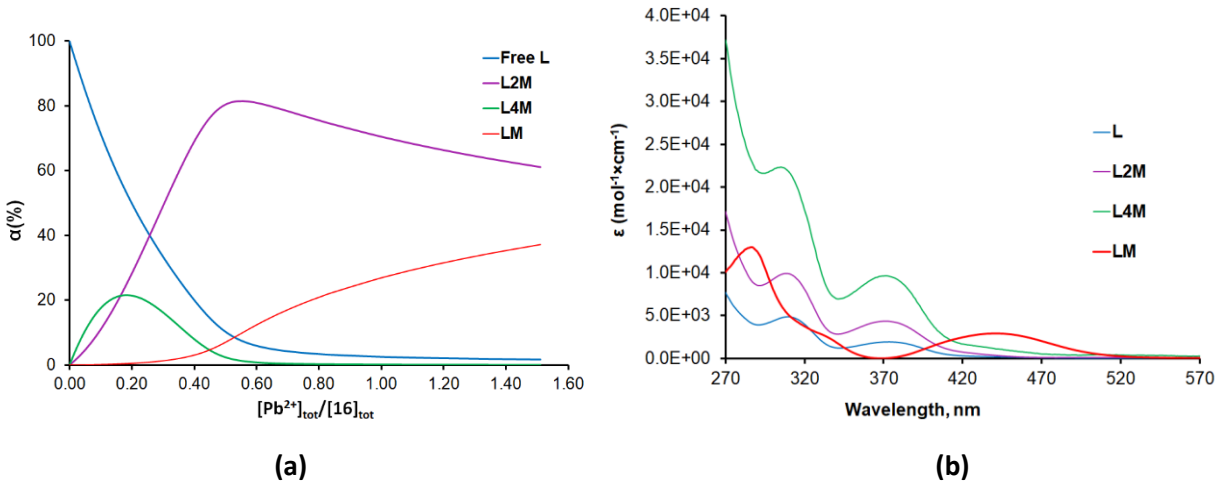


Figure S8. (a) Species distribution diagram for the **16**/Pb^{2+} system in MeCN calculated using Hyperquad program. (b) UV–vis spectra of **16**, $[Pb(\mathbf{16})_4]^{2+}$, $[Pb(\mathbf{16})_2]^{2+}$ and $[Pb(\mathbf{16})]^{2+}$ in MeCN calculated using Hyperquad program.

Data were fit with Hyperquad using the following model:

$Pb^{2+} + 4L \leftrightarrows [PbL_4]^{2+}$ ($\log \beta = 17.5(3)$); $Pb^{2+} + 2L \leftrightarrows [PbL_2]^{2+}$ ($\log \beta = 10.27(1)$);

$Pb^{2+} + L \leftrightarrows [PbL]^{2+}$ ($\log \beta = 5.05(1)$)

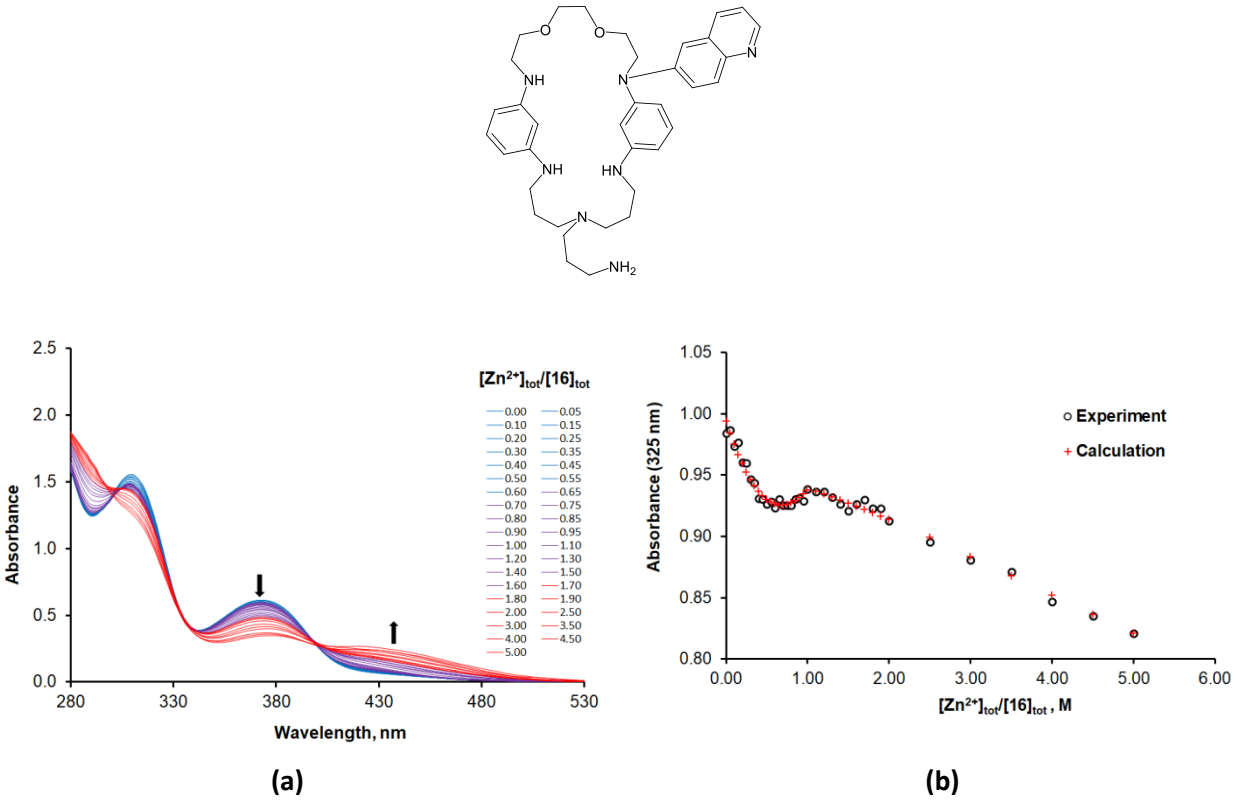


Figure S9. (a) Evolution of the UV–vis absorption spectrum of **16** ($[\mathbf{16}]_{tot}$ = 318 μM, MeCN) upon addition of $Zn(ClO_4)_2$ (0–5 equiv.). (b) Changes of the absorbance as a function of the $[Zn^{2+}]_{tot}/[\mathbf{16}]_{tot}$ ratio at λ = 320 nm.

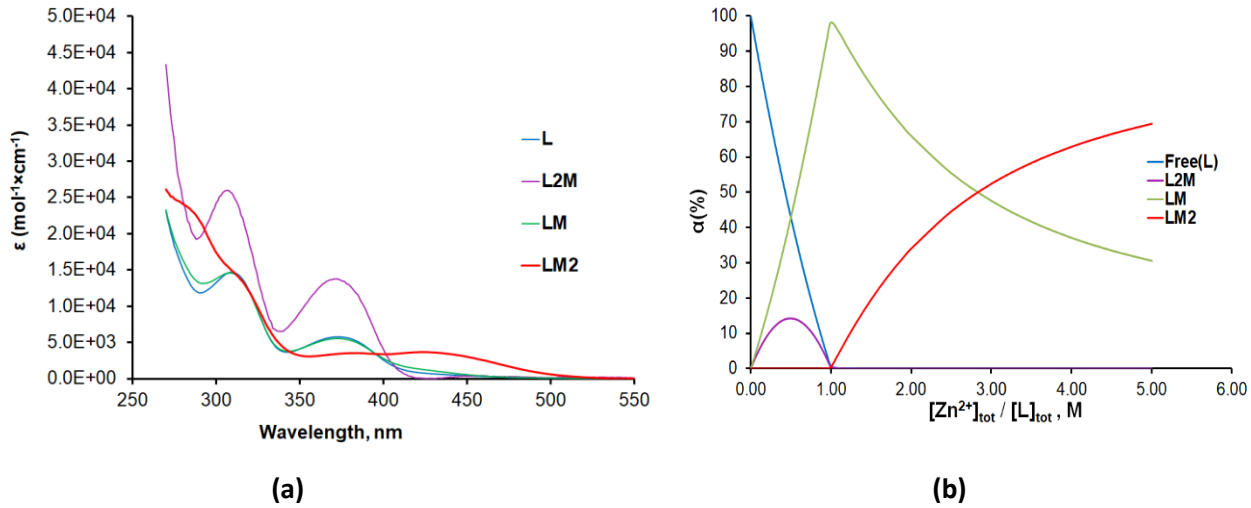


Figure S10. (a) UV–vis spectra of **16**, $[Zn(\mathbf{16})_2]^{2+}$, $[Zn(\mathbf{16})]^{2+}$ and $[Zn_2(\mathbf{16})]^{4+}$ in MeCN calculated using Hyperquad program. (b) Species distribution diagram for the **16**/Zn^{2+} system in MeCN calculated using Hyperquad program.

Data were fit with Hyperquad using the following model:

$Zn^{2+} + 2L \leftrightarrows [ZnL_2]^{2+}$ ($\log\beta = 11.88(3)$);

$Zn^{2+} + L \leftrightarrows [ZnL]^{2+}$ ($\log\beta = 8.31(3)$)

$2Zn^{2+} + L \leftrightarrows [Zn_2L]^{2+}$ ($\log\beta = 12.2(3)$)

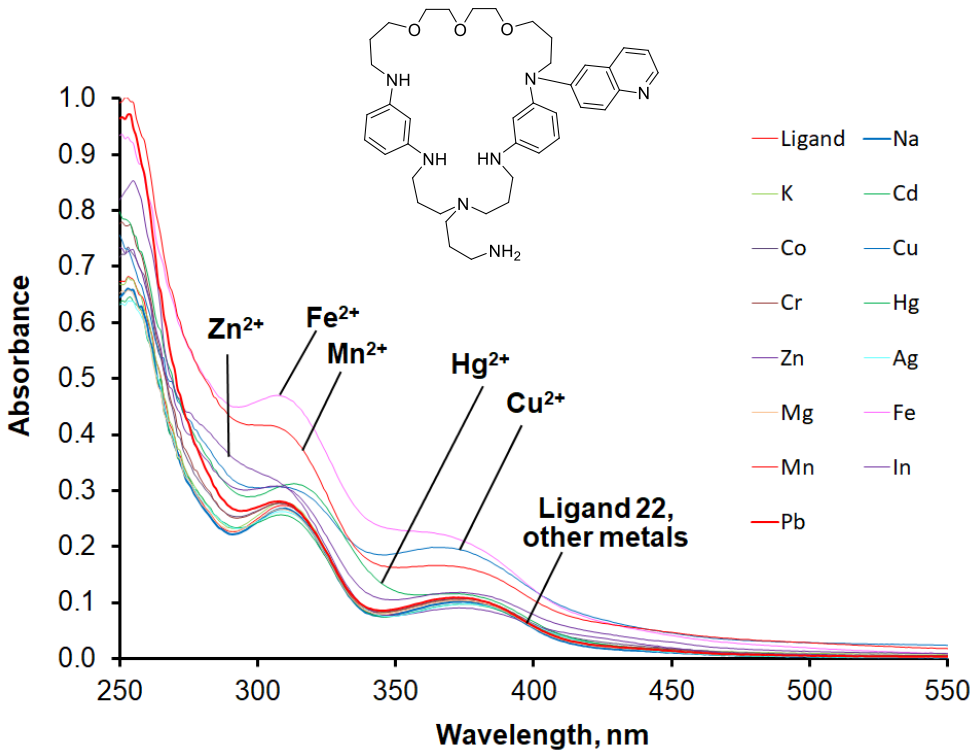


Figure S11. UV-vis spectra of compound **22** in acetonitrile in the presence of Li(I), Na(I), K(I), Mg(II), Ca(II), Ba(II), Al(III), Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Pb(II), Ag(I), Ga(III), In(III), Y(III) (5 equiv.). C_L 1.43*10^{-5} M.

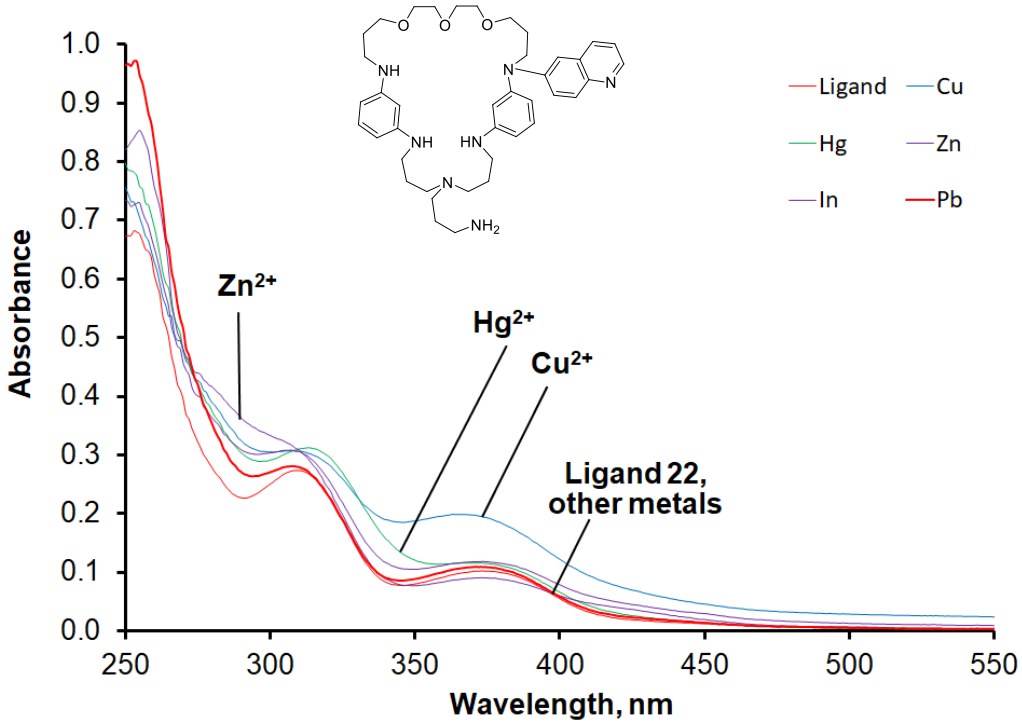


Figure S12. UV-vis spectra of compound **22** in acetonitrile in the presence of selected metal cations: Cu(II), Hg(II), Zn(II), Pb(II), In(III) (5 equiv.). C_L 14.3 μM.

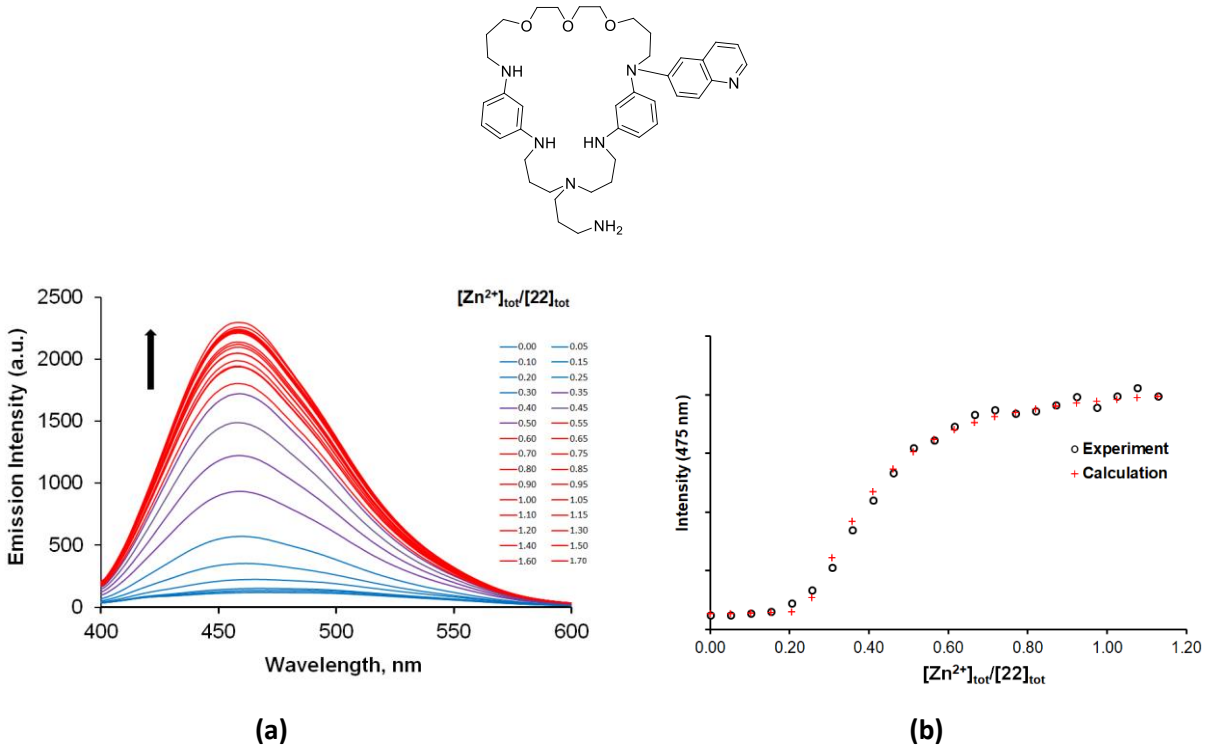


Figure S13. (a) Evolution of the emission spectrum of **22** ($[\mathbf{22}]_{tot}$ = 39 μM, λ_{ex} =380 nm, MeCN) upon addition of $Zn(ClO_4)_2$ (0–1.7 equiv.). (b) Changes of the emission intensity as a function of the $[Zn^{2+}]_{tot}/[\mathbf{22}]_{tot}$ ratio at λ =475 nm.

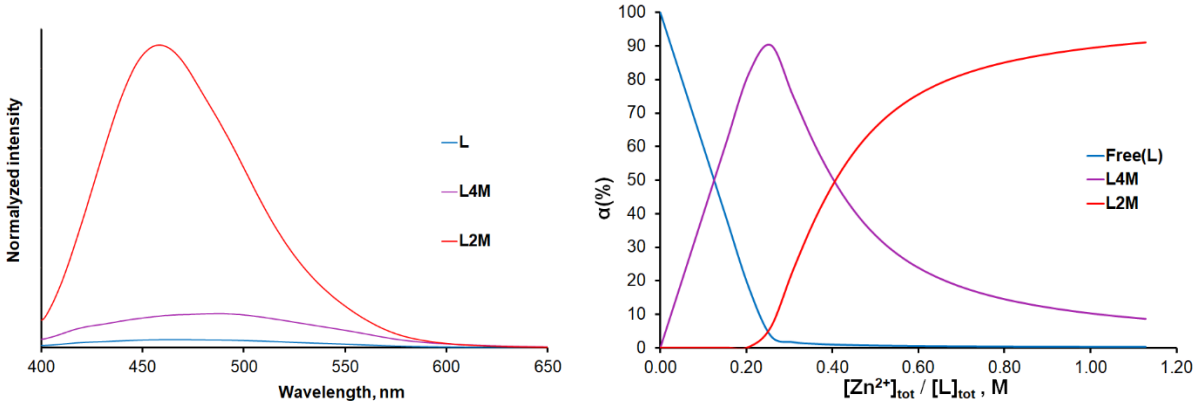


Figure S14. (a) Emission spectra of **22**, $[Zn(\mathbf{22})_4]^{2+}$ and $[Zn(\mathbf{22})_2]^{2+}$ in MeCN calculated using Hyperquad program. (b) Species distribution diagram for the **22**/Zn^{2+} system in MeCN calculated using Hyperquad program.

Data were fit with Hyperquad using the following model:

$Zn^{2+} + 4L \leftrightarrows [ZnL_4]^{2+}$ (log β = 28.2(1));

$Zn^{2+} + 2L \leftrightarrows [ZnL_2]^{2+}$ (log β = 14.69(7))

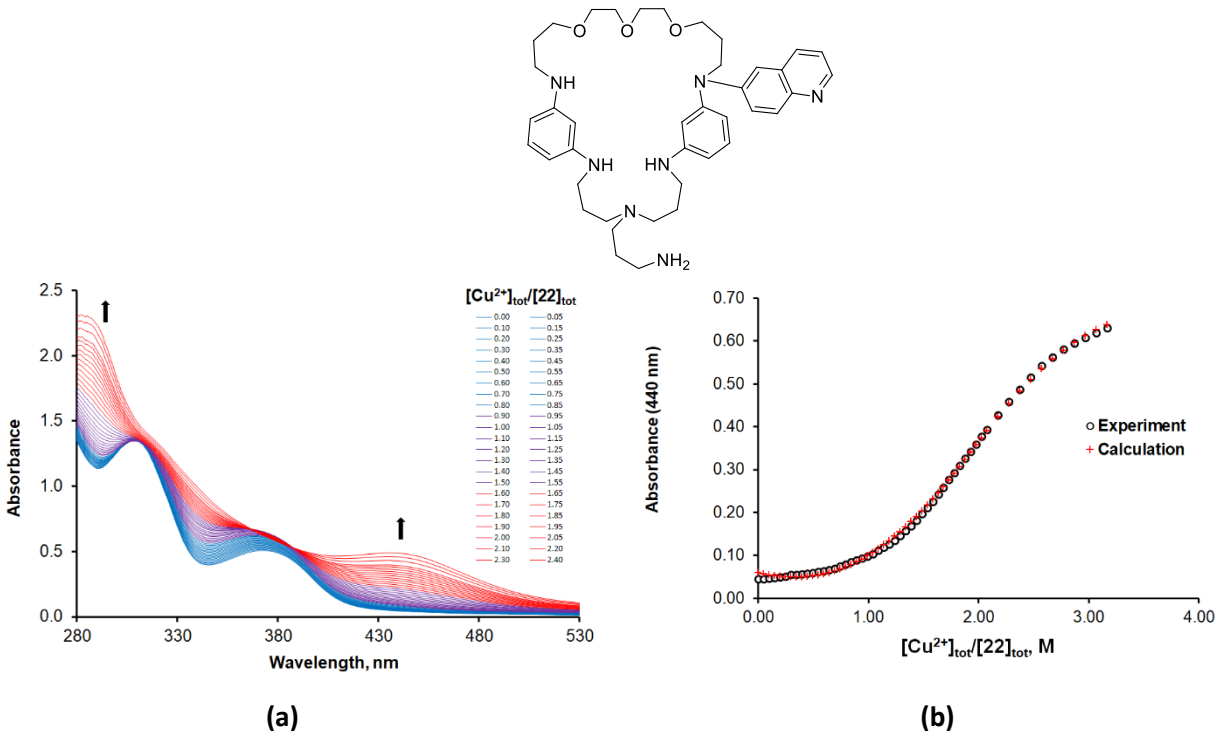


Figure S15. (a) Evolution of the UV–vis absorption spectrum of **22** ($[\mathbf{22}]_{tot}$ = 191 μM, MeCN) upon addition of $Cu(ClO_4)_2$ (0–2 equiv.). (b) Changes of the absorbance as a function of the $[Cu^{2+}]_{tot}/[\mathbf{22}]_{tot}$ ratio at λ =440 nm.

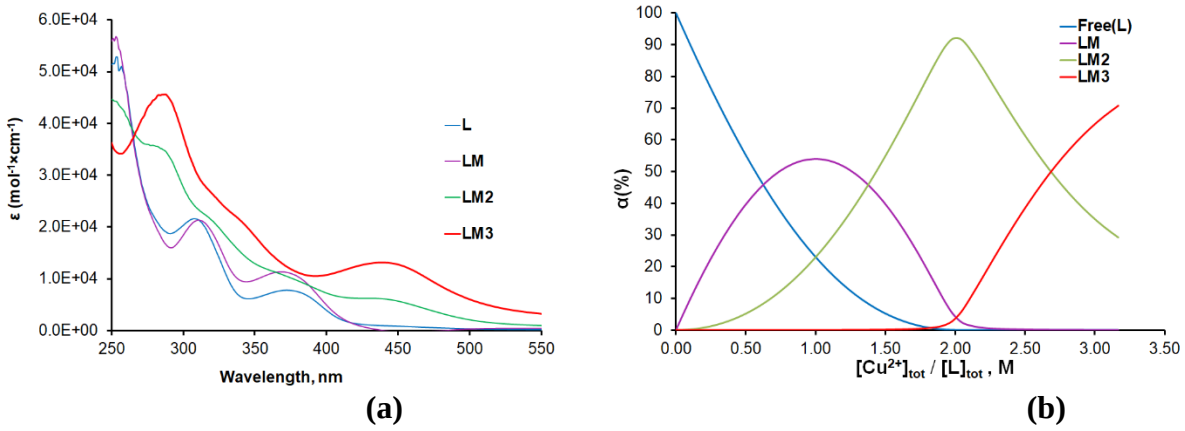


Figure S16. (a) UV–vis spectra of **22**, $[Cu(\mathbf{22})]^{2+}$, $[Cu_2(\mathbf{22})]^{4+}$, $[Cu_3(\mathbf{22})]^{6+}$ in MeCN calculated using Hyperquad program. (b) Species distribution diagram for the **22**/Cu^{2+} system in MeCN calculated using Hyperquad program.

Data were fit with Hyperquad using the following model:

$Cu^{2+} + L \leftrightarrows [CuL]^{2+}$ (log β = 8.45(8))

$2Cu^{2+} + L \leftrightarrows [Cu_2L]^{4+}$ (log β = 16.1(1))

$3Cu^{2+} + L \leftrightarrows [Cu_3L]^{6+}$ (log β = 21.1(2))

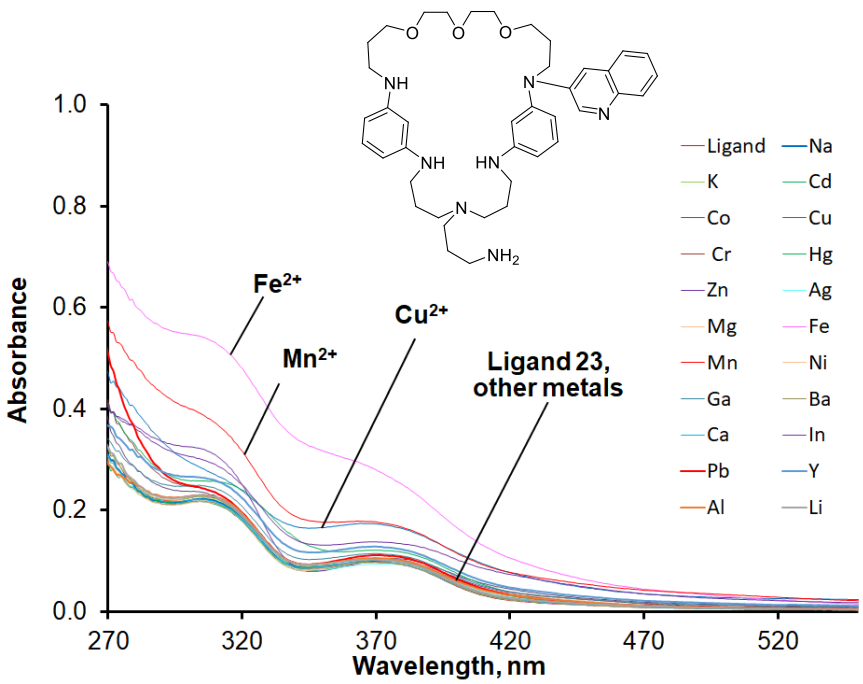


Figure S17. UV-vis spectra of compound **23** in the presence of Li(I), Na(I), K(I), Mg(II), Ca(II), Ba(II), Al(III), Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Pb(II), Ag(I)), Ga(III), In(III), Y(III) (5 equiv.). C_L 21.2 μM.

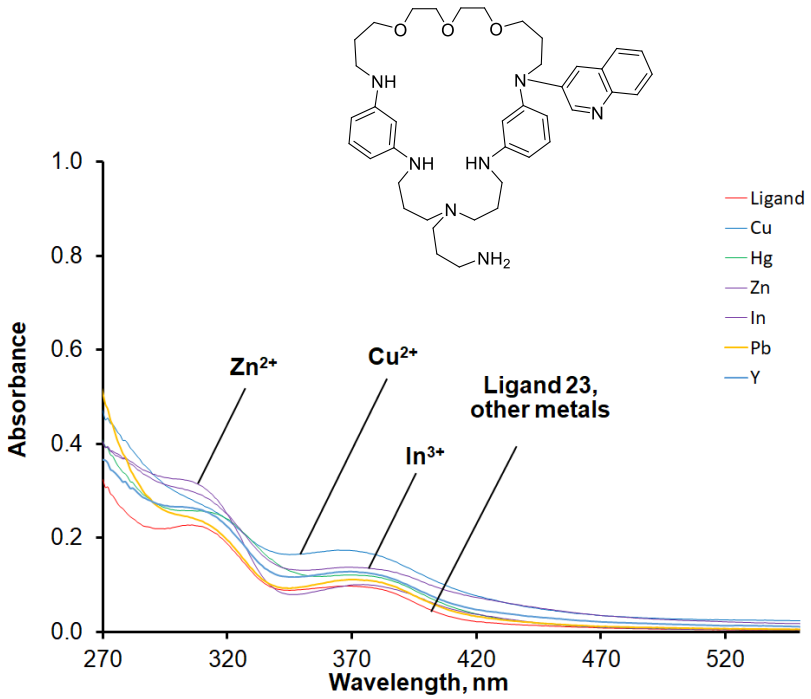


Figure S18. UV-vis spectra of compound **23** in the presence of selected metal cations: Cu(II), Hg(II), Mn(II), Zn(II), Pb(II), In(III), Y(III) (5 equiv.). C_L 21.2 μM.

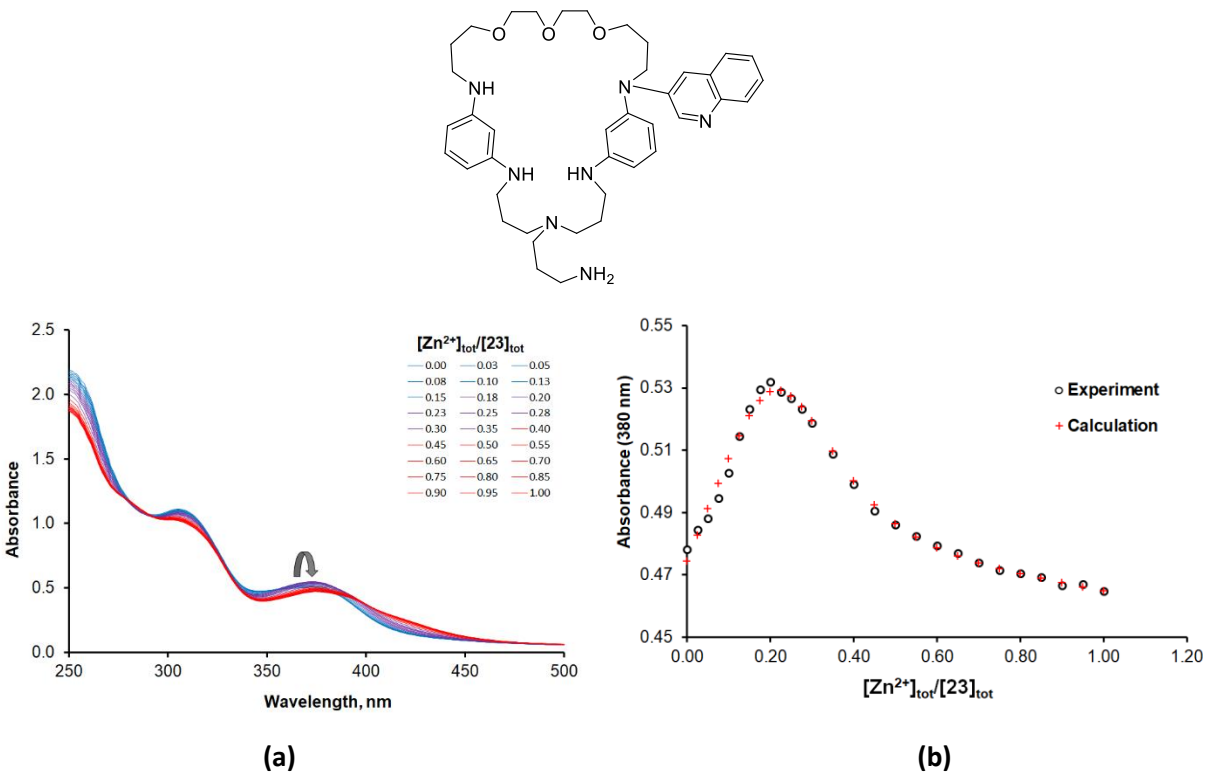


Figure S19. (a) Evolution of the UV–vis absorption spectrum of **23** ($[\mathbf{23}]_{tot}$ = 252 μM, MeCN) upon addition of $Zn(ClO_4)_2$ (0–1 equiv.). (b) Changes of the absorbance as a function of the $[Zn^{2+}]_{tot}/[\mathbf{23}]_{tot}$ ratio at λ =380 nm.

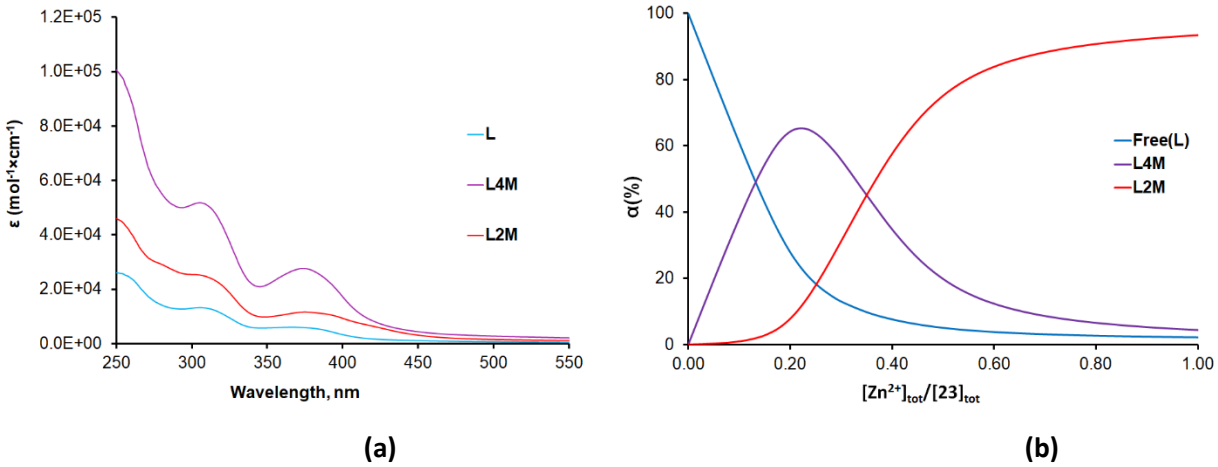
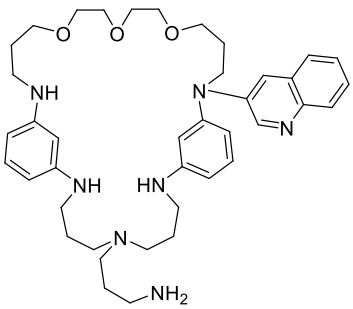


Figure S20. (a) UV–vis spectra of **23**, $[Zn(\mathbf{23})_4]^{2+}$ and $[Zn(\mathbf{23})_2]^{2+}$ in MeCN calculated using Hyperquad program. (b) Species distribution diagram for the **23**/Zn^{2+} system in MeCN calculated using Hyperquad program.

Data were fit with Hyperquad using the following model:

$Zn^{2+} + 4L \leftrightarrows [ZnL_4]^{2+}$ (log β = 21.34(5));

$Zn^{2+} + 2L \leftrightarrows [ZnL_2]^{2+}$ (log β = 11.46(2))



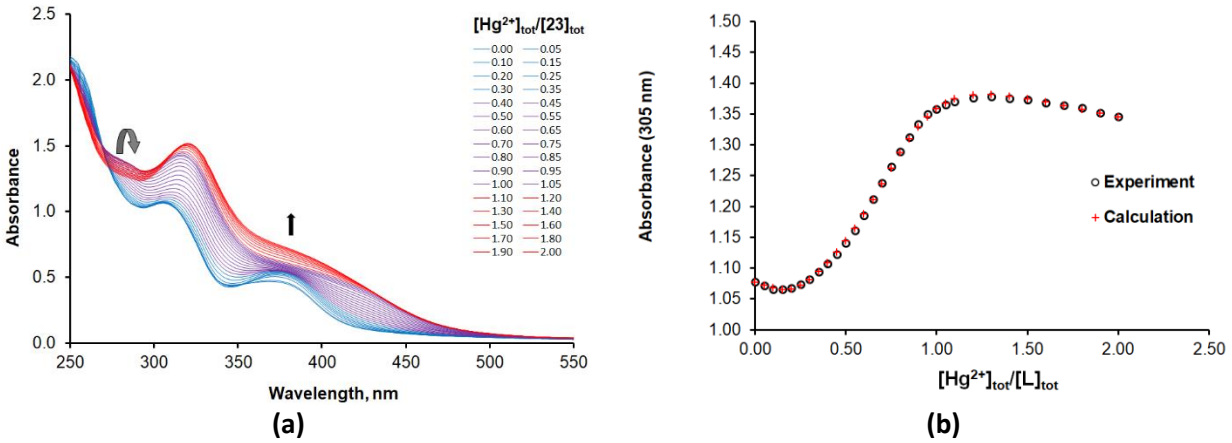


Figure S21. (a) Evolution of the UV–vis absorption spectrum of **23** ([**23**]$_{tot}$ = 252 μM, MeCN) upon addition of $Hg(ClO_4)_2$ (0–2 equiv.). (b) Changes of the absorbance as a function of the [Hg^{2+}]$_{tot}$/[**23**]$_{tot}$ ratio at λ =305 nm.

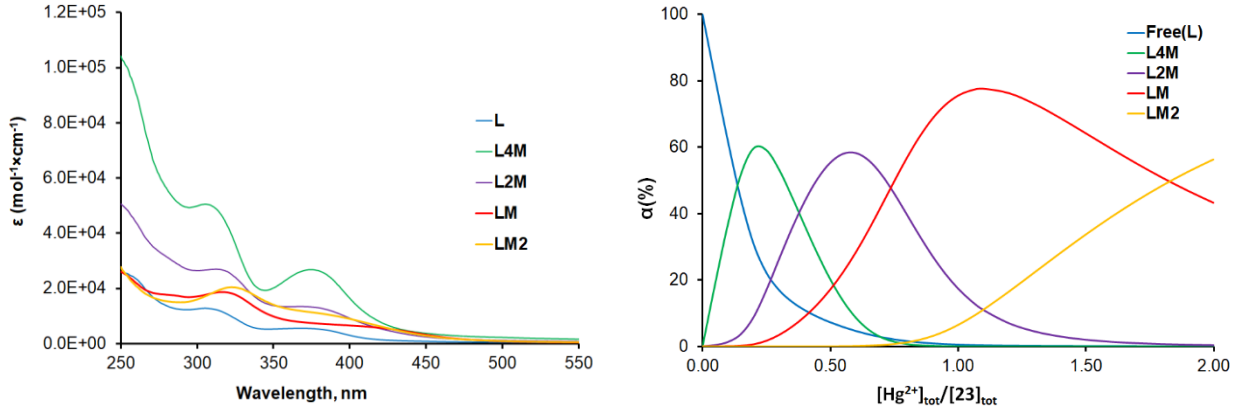


Figure S22. (a) UV–vis spectra of **23**, $[Hg(\mathbf{23})_4]^{2+}$, $[Hg(\mathbf{23})_2]^{2+}$, $[Hg(\mathbf{23})]^{2+}$ and $[Hg_2(\mathbf{23})]^{4+}$ in MeCN calculated using Hyperquad program. (b) Species distribution diagram for the **23**/Hg^{2+} system in MeCN calculated using Hyperquad program.

Data were fit with Hyperquad using the following model:

$Hg^{2+} + 4L \leftrightarrows [HgL_4]^{2+}$ (log β = 22.94(8));

$Hg^{2+} + 2L \leftrightarrows [HgL_2]^{2+}$ (log β = 13.23(7))

$Hg^{2+} + L \leftrightarrows [HgL]^{2+}$ (log β = 7.80(5))

$2Hg^{2+} + L \leftrightarrows [Hg_2L]^{4+}$ (log β = 12.3(1))

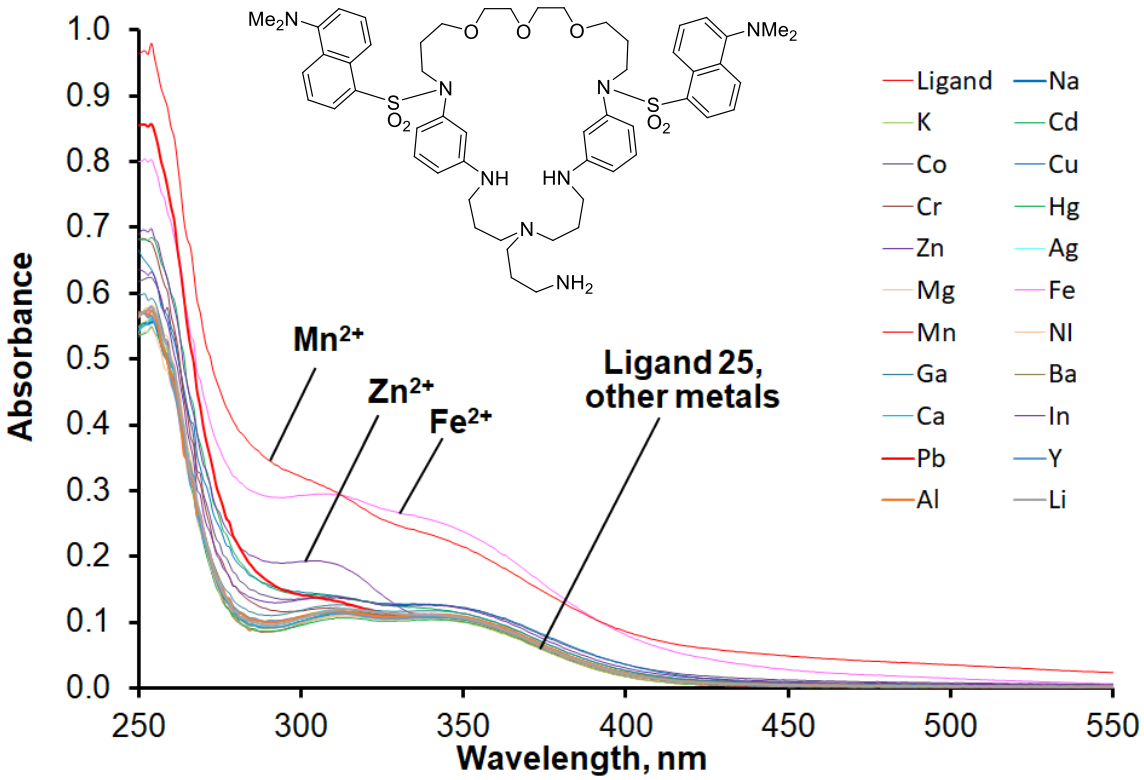


Figure S23. UV-vis spectra of compound **25** in the presence of Li(I), Na(I), K(I), Mg(II), Ca(II), Ba(II), Al(III), Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Pb(II), Ag(I), Ga(III), In(III), Y(III) (5 equiv.). C_L 12.3 μM.

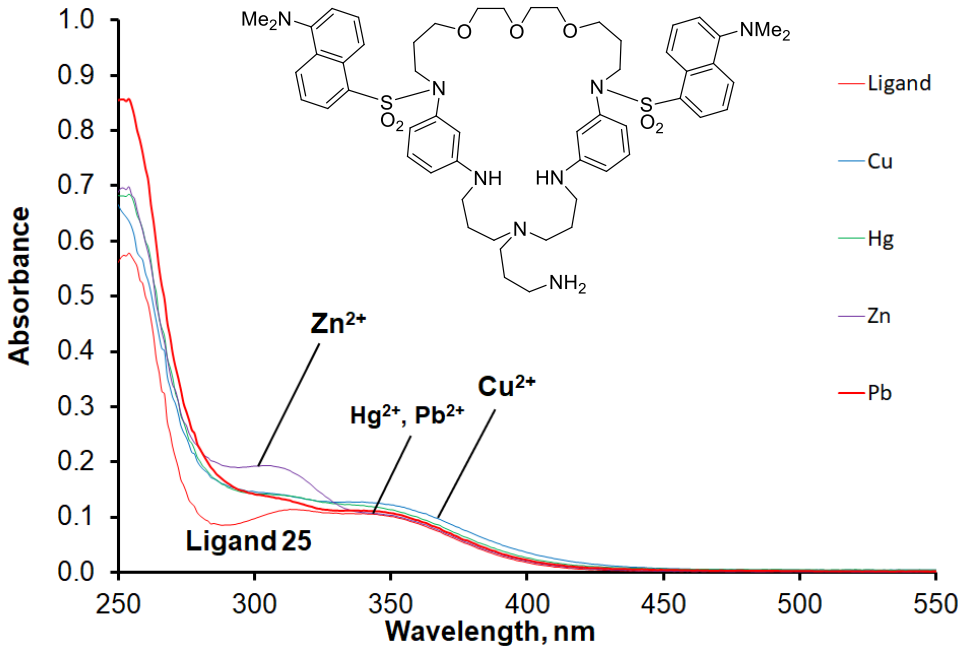
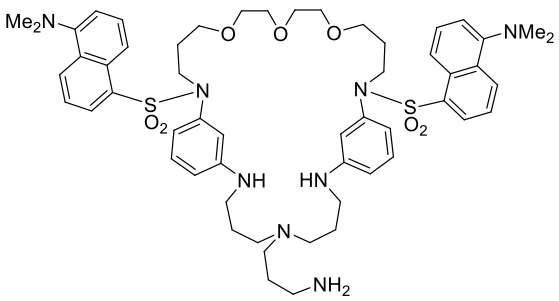
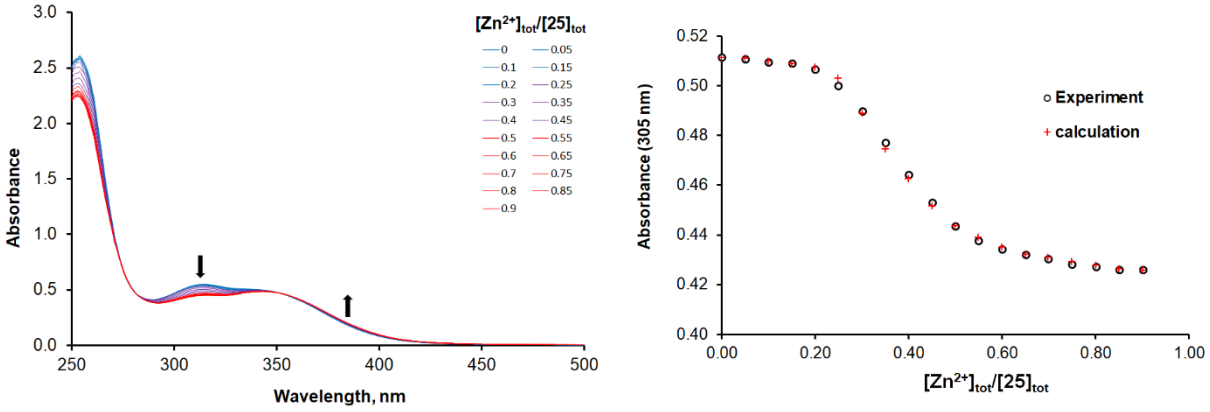


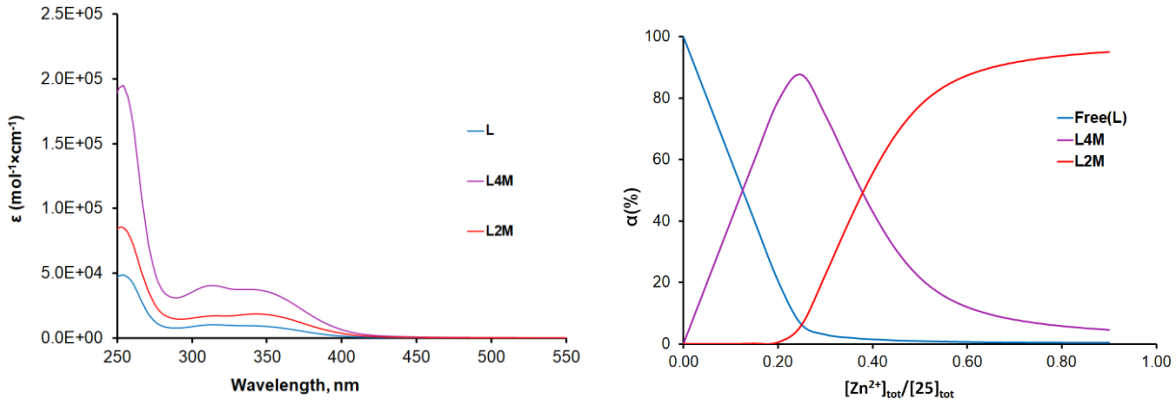
Figure S24. UV-vis spectra of compound **25** in the presence of selected metal cations: Cu(II), Hg(II), Zn(II), Pb(II) (5 equiv.). C_L 12.3 μM.





(a) **(b)**

Figure S25. (a) Evolution of the UV–vis absorption spectrum of **25** ($[\mathbf{25}]_{tot}$ = 160 μM, MeCN) upon addition of $Zn(ClO_4)_2$ (0–1 equiv.). (b) Changes of the absorbance as a function of the $[Zn^{2+}]_{tot}/[\mathbf{25}]_{tot}$ ratio at λ =320 nm.



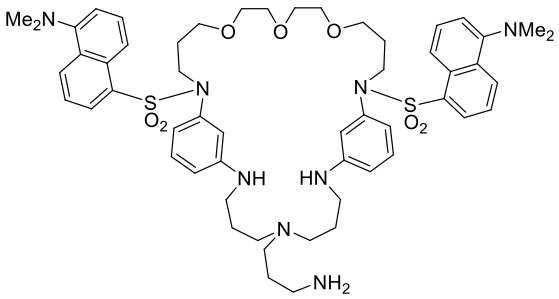
(a) **(b)**

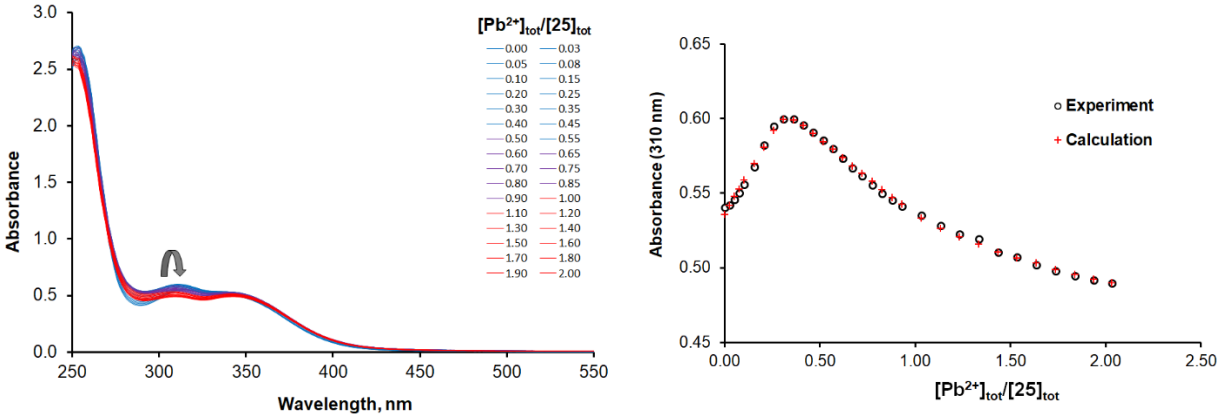
Figure S26. (a) UV–vis spectra of **25**, $[Zn(\mathbf{25})_4]^{2+}$ and $[Zn(\mathbf{25})_2]^{2+}$ in MeCN calculated using Hyperquad program. (b) Species distribution diagram for the **25**/Zn^{2+} system in MeCN calculated using Hyperquad program.

Data were fit with Hyperquad using the following model:

$Zn^{2+} + 4L \leftrightarrows [ZnL_4]^{2+}$ (log β = 25.3(1));

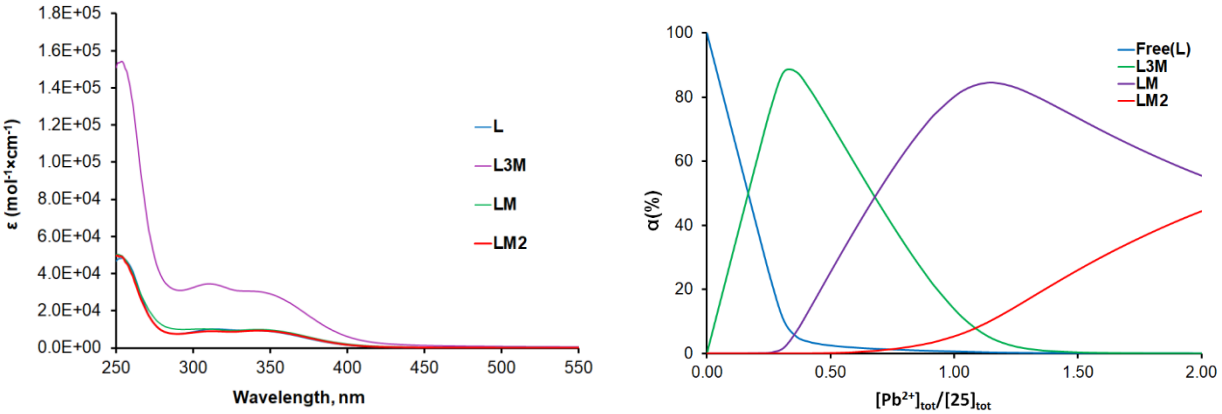
$Zn^{2+} + 2L \leftrightarrows [ZnL_2]^{2+}$ (log β = 13.49(5))





(a) **(b)**

Figure S27. (a) Evolution of the UV–vis absorption spectrum of **25** ($[\mathbf{25}]_{tot}$ = 160 μM, MeCN) upon addition of $Pb(ClO_4)_2$ (0–5 equiv.). (b) Changes of the absorbance as a function of the $[Pb^{2+}]_{tot}/[\mathbf{25}]_{tot}$ ratio at λ =310 nm.



(a) **(b)**

Figure S28. (a) UV–vis spectra of **25**, $[Pb(\mathbf{25})_3]^{2+}$, $[Pb(\mathbf{25})]^{2+}$ and $[Pb_2(\mathbf{25})]^{4+}$ in MeCN calculated using Hyperquad program. (b) Species distribution diagram for the **25**/Pb^{2+} system in MeCN calculated using Hyperquad program.

Data were fit with Hyperquad using the following model:

$Pb^{2+} + 3L \leftrightarrows [PbL_3]^{2+}$ ($\log \beta = 19.48(5)$);

$Pb^{2+} + L \leftrightarrows [PbL]^{2+}$ ($\log \beta = 7.74(2)$)

$2Pb^{2+} + L \leftrightarrows [Pb_2L]^{2+}$ ($\log \beta = 12.1(1)$)

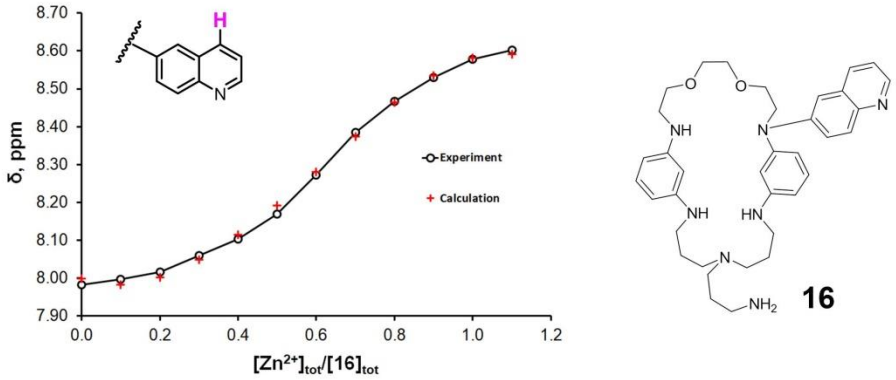


Figure S29. Changes of the chemical shift of H4(Quin) proton in ^{1}H NMR spectrum of **16** upon addition of Zn(II) perchlorate(CD_3CN, 298 K) and calculated chemical shifts.
Data were fit with EQNMR using the following model:
$Zn^{2+} + L \leftrightarrows [ZnL]^{2+}$ (log $\beta > 5$);
$Zn^{2+} + 2L \leftrightarrows [ZnL_2]^{2+}$ (log $\beta > 5$);

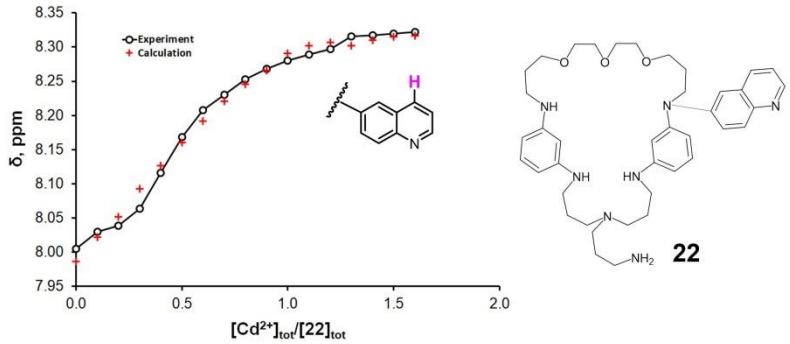


Figure S30. Changes of the chemical shift of H4(Quin) proton in ^{1}H NMR spectrum of **22** upon addition of Cd(II) perchlorate(CD_3CN, 298 K) and calculated chemical shifts.
Data were fit with EQNMR using the following model:
$Cd^{2+} + L \leftrightarrows [CdL]^{2+}$ (log $\beta = 3.1(2)$);
$Cd^{2+} + 2L \leftrightarrows [CdL_2]^{2+}$ (log $\beta = 2.7(3)$);

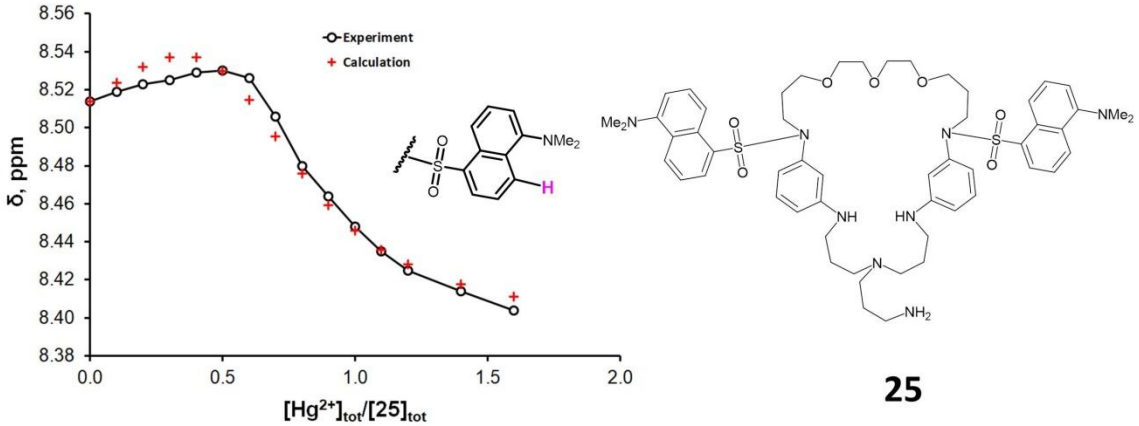


Figure S31. Changes of the chemical shift of H4(Quin) proton in ^{1}H NMR spectrum of **25** upon addition of Hg(II) perchlorate(CD_3CN, 298 K) and calculated chemical shifts.
Data were fit with BindFit using the following model:
$Hg^{2+} + L \leftrightarrows [HgL]^{2+}$ (log $\beta = 3.7(2)$);
$Hg^{2+} + 2L \leftrightarrows [HgL_2]^{2+}$ (log $\beta = 2.5(2)$);