# Supporting Information for

# Absorption and Fluorescence Emission Investigations on Supramolecular Assemblies of Tetrakis-(4-sulfonatophenyl)porphyrin and Graphene Quantum Dots

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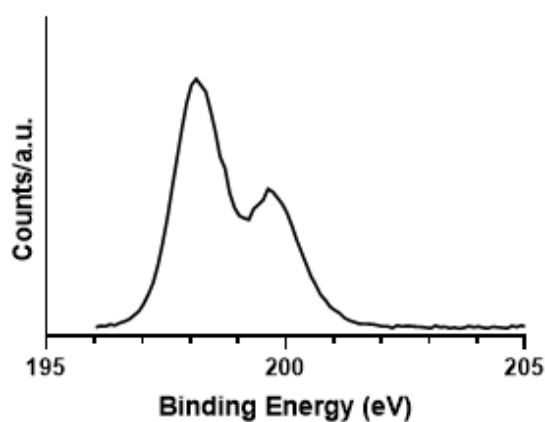
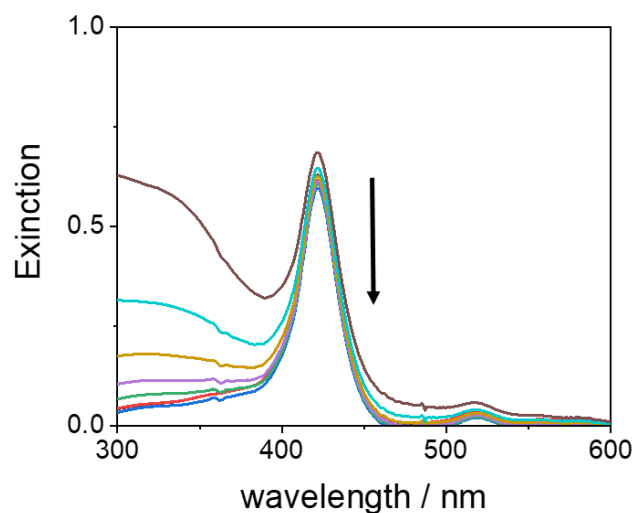**Figure S1.** XPS spectra for Cl2p levels region on GQD.

**Figure S2.** UV/Vis extinction spectral changes during the titration of TMPyP(4)$^{4+}$ with GQDs at neutral pH (the arrow marks the increasing GQDs concentration). Experimental conditions: [TMPyP(4)$^{4+}$] = 3 μM; [GQDs] = 0, 0.002, 0.01, 0.034, 0.056, 0.1, 0.18, 0.40 mg/mL; phosphate buffer 1 mM, pH = 7; T = 298 K; cell path length 1 cm.



**Figure S3.** Fluorescence emission spectral changes during the titration of TMPyP(4)$^{4+}$ with GQDs at neutral pH (the arrow marks the increasing GQDs concentration). The emission spectra are not corrected for the extinction of the samples. Experimental conditions: [TMPyP(4)$^{4+}$] = 3 μM; [GQDs] = 0, 0.002, 0.01, 0.034, 0.056, 0.1, 0.18, 0.40 mg/mL; phosphate buffer 1 mM, pH = 7; T = 298 K; cell path length 1 cm.
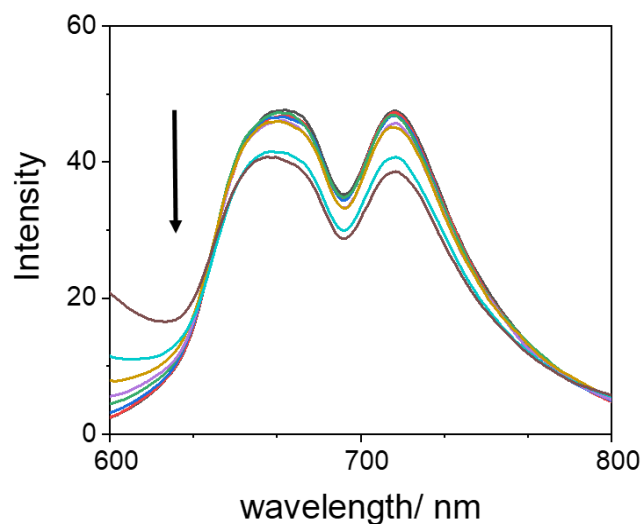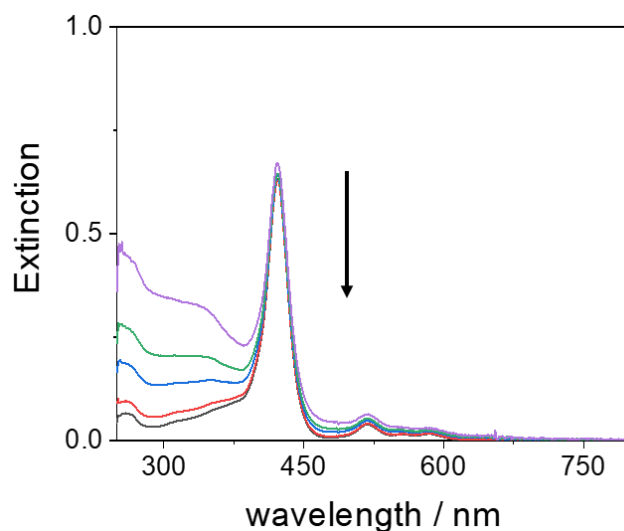
**Figure S4.** UV/Vis extinction spectral changes during the titration of TMPyP(4)[4+] with GQDs at pH = 3 (the arrow marks the increasing GQDs concentration). Experimental conditions: [TMPyP(4)[4+]] = 3 μM; [GQDs] = 0, 0.01, 0.056, 0.1, – 0.18 mg/mL; [HCl] = 10^{-3} M; T = 298 K; cell path length 1 cm.
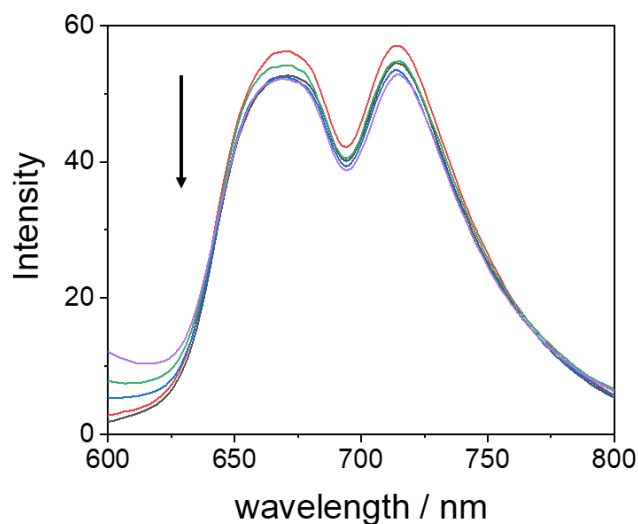


**Figure S5.** Fluorescence emission spectral changes during the titration of TMPyP(4)[4+] with GQDs at pH = 3 (the arrow marks the increasing GQDs concentration). The emission spectra are not corrected for the extinction of the samples. Experimental conditions: [TMPyP(4)[4+]] = 3 μM; [GQDs] = 0, 0.01, 0.056, 0.1, – 0.18 mg/mL; [HCl] = 10^{-3} M; T = 298 K; cell path length 1 cm.

**Table S1.** Fluorescence lifetimes ($\tau_1$ and $\tau_2$) and relative percentage amplitudes, together with the time constant of fluorescence anisotropy decays for the titration of $TPPS_4^{4-}$ with GQDs at neutral pH. Experimental conditions: $[TPPS_4^{4-}]$ = 3 µM; phosphate buffer 10 mM, pH = 7; T = 298 K; cell path length 1 cm; $\lambda_{exc}$ = 390 nm; $\lambda_{em}$ = 644 nm.

| [GQDs] / mg mL⁻¹ | Lifetime / ns (relative amplitude) | | Anisotropy Decays / ns |
|---|---|---|---|
| 0 | $\tau_1$ = 10.0 ± 0.1 (97%) | $\tau_2$ = 1.1 ± 0.1 (3%) | $\tau_r$ = 0.72 ± 0.1 |
| 0.02 | $\tau_1$ = 10.4 ± 0.1 (93%) | $\tau_2$ = 1.3 ± 0.1 (7%) | $\tau_r$ = 0.96 ± 0.1 |
| 0.04 | $\tau_1$ = 9.99 ± 0.1 (92%) | $\tau_2$ = 1.4 ± 0.1 (8%) | $\tau_r$ = 1.00 ± 0.1 |
| 0.06 | $\tau_1$ = 10.1 ± 0.1 (86%) | $\tau_2$ = 1.8 ± 0.1 (14%) | $\tau_r$ = 0.92 ± 0.1 |

**Table S2.** Fluorescence lifetimes ($\tau_1$ $\tau_2$ and $\tau_3$) and relative percentage amplitudes for the titration of GQDs with $TPPS_4^{4-}$ at neutral pH. Experimental conditions: [GQDs] = 0.14 mg/mL; phosphate buffer 10 mM, pH = 7; T = 298 K; cell path length 1 cm; $\lambda_{exc}$ = 390 nm; $\lambda_{em}$ = 474 nm.

| [TPPS₄] / µM | Lifetime / ns (relative amplitude) | | |
|---|---|---|---|
| 0 | $\tau_1$= 15.4 ± 0.1 (14%) | $\tau_2$=5.4 ± 0.1 (61%) | $\tau_3$=1.8 ± 0.1 (25%) |
| 0.07 | $\tau_1$= 14.6 ± 0.1 (17%) | $\tau_2$=5.0 ± 0.1 (64%) | $\tau_3$=1.5 ± 0.1 (19%) |
| 0.42 | $\tau_1$= 14.9 ± 0.1 (16%) | $\tau_2$=5.2 ± 0.1 (72%) | $\tau_3$=1.6 ± 0.1 (22%) |
| 0.90 | $\tau_1$= 15.5 ± 0.1 (15%) | $\tau_2$=5.3 ± 0.1 (61%) | $\tau_3$=1.8 ± 0.1 (24%) |
| 1.80 | $\tau_1$= 16.3 ± 0.1 (14%) | $\tau_2$=5.4 ± 0.1 (64%) | $\tau_3$=1.7 ± 0.1 (22%) |
| 3.00 | $\tau_1$= 16.5 ± 0.1 (15%) | $\tau_2$=5.6 ± 0.1 (63%) | $\tau_3$=1.9 ± 0.1 (22%) |

**Table S3.** Fluorescence lifetimes ($\tau_1$ and $\tau_2$) and relative percentage amplitudes, together with the time constant of fluorescence anisotropy decays for the titration of $TPPS_4^{4-}$ with GQDs at pH = 3. Experimental conditions: $[TPPS_4^{4-}]$ = 3 µM; pH = 3 ([HCl] = 10⁻³ M); T = 298 K; cell path length 1 cm; $\lambda_{exc}$ = 390 nm; $\lambda_{em}$ = 670 nm.

| [GQDs] / mg mL⁻¹ | Lifetime / ns (relative amplitude) | | Anisotropy Decays / ns |
|---|---|---|---|
| 0 | $\tau_1$ = 3.9 ± 0.1 (92%) | $\tau_2$ = 1.9 ± 0.1 (8%) | $\tau_r$ = 0.88 ± 0.1 |
| 0.02 | $\tau_1$ = 3.8 ± 0.1 (90%) | $\tau_2$ = 1.9 ± 0.1 (10%) | $\tau_r$ = 0.99 ± 0.1 |
| 0.08 | $\tau_1$ = 3.8 ± 0.1 (90%) | $\tau_2$ = 1.9 ± 0.1 (10%) | $\tau_r$ = 1.02 ± 0.1 |
| 0.28 | $\tau_1$ = 3.9 ± 0.1 (92%) | $\tau_2$ = 1.9 ± 0.1 (10%) | $\tau_r$ = 1.05 ± 0.1 |