Light activated zirconium(IV) phthalocyanine derivatives linked to graphite oxide flakes and discussion on their antibacterial activity

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(1) Lamp used to activate the investigated samples

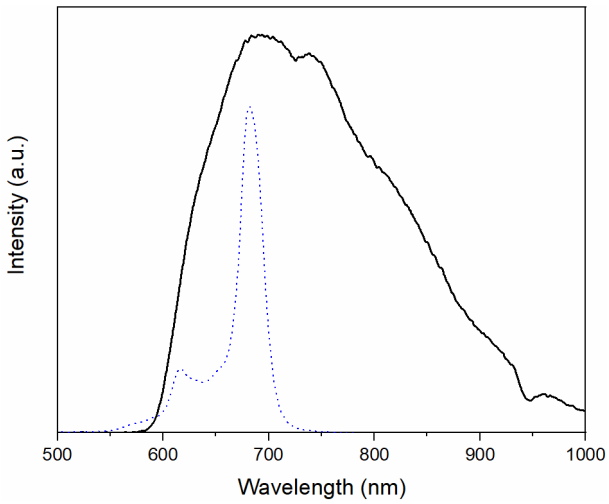
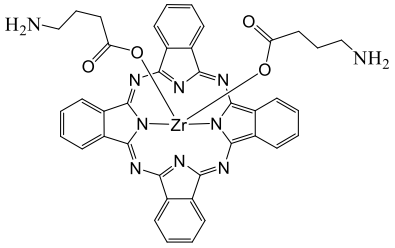


Figure S1. Emission spectrum of the red-NIR lamp used in the experiment. Dotted curve shows absorption spectrum of bis(4-aminobutyrato)ZrPc.

(2) Data of zirconium(IV) phthalocyanines containing out-of-plane ligands: GABA (4-aminobutyric acid) and UDA (11-aminoundecanoic acid)

bis(GABA)ZrPc

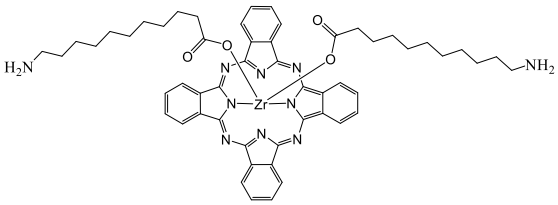


$C_{40}H_{32}N_{10}O_4Zr$ Calcd.: C, 59.46; H, 3.99; N, 17.34; Zr, 11.29. Found: C, 59.49; H, 4.03; N, 17.24; Zr, 11.38.

^{1}H NMR (300 MHz, DMSO-d_6) δ: 9.40 (s, 8H), 8.25 (s, 8H), 3.02 (m, 4H), 1.26 (d, 4H), 1.01-0.43 (m, 8H).

IR (KBr) cm^{-1}: 468, 634, 735, 745, 891, 975, 996, 1025, 1032, 1077, 1154, 1187, 1210, 1241, 1287, 1332, 1398, 1430, 1451, , 1512, 1606, 1639, 2939, 3065, 3478.

bis(UDA)ZrPc



$C_{54}H_{60}N_{10}O_4Zr$ Calcd.: C, 64.58; H, 6.02; N, 13.95; Zr, 9.08. Found: C, 64.34; H, 6.08; N, 13.74; Zr, 9.17.

^{1}H NMR (300 MHz, DMSO-d_6) δ: 9.45 (m, 8H), 8.22-8.18 (m, 8H), 3.69 (t, 4H), 172-1.60 (m, 8H), 1.34-1.20 (m, 10H), 1.12-1.01 (m, 4H), 0.94-0.84 (m, 4H), 0.67-0.57 (m, 6H), 0.38-0.29 (m, 4H), 0.21-0.11 (m, 4H).

IR (KBr) cm^{-1}: 472, 511, 564, 579, 606, 629, 747, 786, 891, 976, 1012, 1073, 1118, 1211, 1260, 1333, 1429, 1453, 1467, 1518, 1600, 1622, 2947, 3055, 3418, 3463.

(3) Test of ZrPc/GO solubility in DMSO

Selected complex of ZrPc deposited on GO was dispersed using ultrasounds in dimethyl sulfoxide. The absorption spectrum was measured just after preparation, one hour later, and after removing suspended powder by centrifugation. Slight decrease of absorption level after one hour showed instability of the suspension (gradual sedimentation of the flakes). The absorbance decreased significantly after centrifugation. Nevertheless, the absorption of ZrPc in red region and the edge of absorption band in the UV-blue range indicated that the flakes with ZrPc was partially dissolved and could not be removed from the solvent.

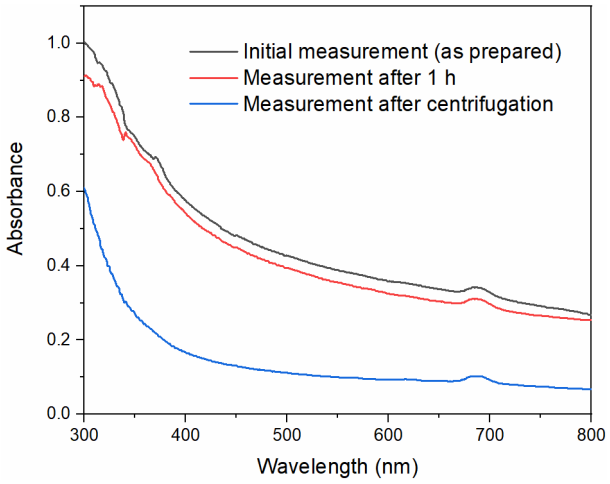


Figure S2. Absorption spectra of ZrPc/GO before and after centrifugation.

(4) Test of singlet oxygen generation by GO

The graphite oxide suspension was mixed with DPBF indicator and was kept under lamp irradiation. After 2 and 4 min, the absorption spectra were recorded (Fig. S1). No changes in the DPBF band intensity in the presence of GO and irradiation indicate that no singlet oxygen species were formed.

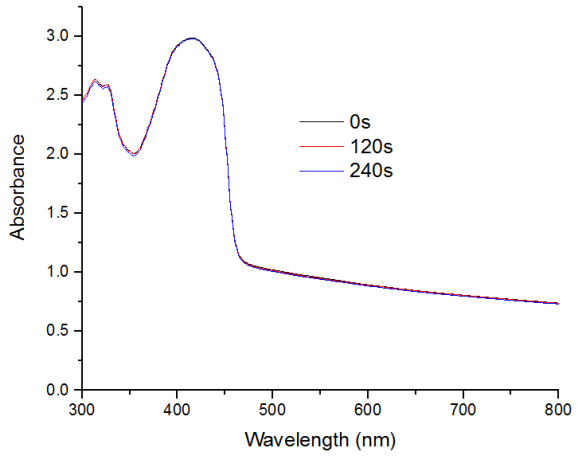


Figure S3. Absorption spectra of DPBF in the presence of 1,3-diphenylisobenzofuran before and after 2 or 4 min of lamp irradiation.

(5) Results of antimicrobial test of bis(GABA)ZrPc/GO and bis(UDA)ZrPc/GO against two *E. coli* strains

Table S1. MIC and MBC values of composites against tested bacteria strains. Irradiation time 5 means permanent irradiation during 5 min whereas, 10 means 5 fold 2 min irradiation with 1 min break.

Irradiation time (min):	0	0	5	5	10	10
Concentration (μg/mL):	MIC	MBC	MIC	MBC	MIC	MBC
E. coli 6.2E						
bis(GABA)ZrPc/GO	>8192	>8192	>8192	>8192	>8192	>8192
bis(UDA)ZrPc/GO	>8192	>8192	>8192	>8192	>8192	>8192
E. coli J53						
bis(GABA)ZrPc/GO	>8192	>8192	>8192	>8192	>8192	>8192
bis(UDA)ZrPc/GO	>8192	>8192	>8192	>8192	>8192	>8192