

Electronic Supplementary Information

Design of porphyrin-based conjugated microporous polymers with enhanced singlet oxygen productivity

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Content

Synthetic procedures

Table S1. Elemental analysis of CMPs.

Scheme S1. Synthetic procedures of CMP precursors.

Figure S1. ^{13}C MAS-NMR spectra of CMPs.

Figure S2. FTIR of CMPs.

Figure S3-S7. TGA/DTA curves and the evolution of gases for CMP samples.

Figure S8. Adsorption isotherms of nitrogen at 77 K.

Figure S9. NLDFT pore size distribution calculated from the nitrogen adsorption isotherms.

Figure S10. Normalized absorption spectra of CMPs in acetonitrile dispersions.

Figure S11. Normalized absorption spectra of 2D-PdTPP and 3D-PdTPP in acetonitrile dispersions.

Figure S12. Luminescence emission spectra of 2D-PdTPP dispersions in acetonitrile.

Figure S13. Luminescence emission spectra of photosensitized $\text{O}_2(^1\Delta_g)$ produced by 2D-PdTPP and 3D-PdTPP in air atmosphere.

Figure S14. Luminescence emission spectra of photosensitized $\text{O}_2(^1\Delta_g)$ produced in acetonitrile dispersions of 2D-PdTPP.

Figure S15. Luminescence emission spectra of photosensitized $\text{O}_2(^1\Delta_g)$ produced in acetonitrile dispersions of 3D-TTP.

Figure S16. Luminescence emission spectra of photosensitized $\text{O}_2(^1\Delta_g)$ produced in acetonitrile dispersions of 3D-DPP.

Figure S17. Reaction of photosensitized $\text{O}_2(^1\Delta_g)$ produced by 3D-PdTPP dispersions in acetonitrile with 9,10-diphenylanthracene.

Synthetic procedures (see also Scheme S1)

Preparation of tetrakis(4-bromophenyl)methane (1).¹ A two-necked round-bottom flask connected via a rubber hose with a washing flask filled with 20% water solution of NaOH was charged with tetraphenylmethane (4.50 g; 12.5 mmol) and 10 mL of liquid Br₂ was added under vigorous stirring. After 20 min, the mixture was poured onto 40 mL of EtOH cooled to -78 °C. The resulting yellowish slurry was filtered and thoroughly washed with a saturated Na₂S₂O₅ water solution. The crude product was recrystallized from a 1:1 mixture of CHCl₃ and EtOH. Yield: 3.882 g, 49 %.

¹H NMR (CDCl₃): δ 7.01 (d, ³J_{HH} = 8.8 Hz, 8H); 7.39 (d, ³J_{HH} = 8.8 Hz, 8H).

Preparation of tetrakis(4-boronylphenyl)methane (2).² A Schlenk tube charged with **1** (1.27 g; 2.0 mmol) was evacuated, purged three times with Ar, followed by the addition of dry THF (120 mL). The solution was cooled in a CO₂(s)/EtOH bath, and BuLi (6.5 mL of 2.5 M solution in hexane; 16 mmol) was dropwise added under vigorous stirring. After 30 min, B(O-*i*Pr)₃ (5.5 mL; 238 mmol) was added and the mixture was further stirred for 20 min in the cooling bath and 60 min after the removal from the bath. The reaction was quenched by the addition of 25 mL of 1 M HCl. The crude mixture was concentrated on a rotavapor, neutralized with 1 M NaOH, and filtered. The pure product was obtained by acidification with the excess of 1 M HCl, filtration, and thorough washing with water.

Yield: 0.899 g, 91 %.

¹H NMR (CDCl₃): δ 7.14 (d, ³J_{HH} = 8.0 Hz, 8H); 7.68 (d, ³J_{HH} = 8.0 Hz, 8H); 8.03 (s, 8H).

Preparation of phenyldipyrromethane (3).³ A mixture of pyrrole (3.92 mL; 56.5 mmol) and benzaldehyde (1.92 mL; 18.8 mmol) was suspended in diluted HCl (1.6 mL of concentrated HCl in 100 mL) and vigorously stirred for 90 min at room temperature. The resulting slurry was filtered and washed five times with water and hexane.

Yield: 3.0 g, 72 %.

¹H NMR (CDCl₃): δ 5.48 (s, 1H); 5.93 (s, 2H); 6.18 (q, 2H); 6.70 (s, 2H); 7.14 – 7.36 (m, 5H), 7.91 (s, 2H).

Preparation of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (4).⁴ A 100 mL round-bottom flask was charged with 4-formylbenzeneboronic acid (2.00 g; 13.4 mmol) and pinacol (1.88 g; 16.1 mmol). The solids were layered with Et₂O (20 mL) and the slurry

was stirred for 24 hours at room temperature until all the reactants dissolved. The resulting mixture was diluted with Et₂O (40 mL), washed with NaCl solution, and the organic phase was dried over MgSO₄. The product was purified by column chromatography on silica gel using CH₂Cl₂ as an eluent.

Yield: 2.59 g, 83 %.

¹H NMR (CDCl₃): δ 1.36 (s, 12H); 7.87 (d, ³J_{HH} = 8.0 Hz, 2H); 7.96 (d, ³J_{HH} = 8.0 Hz, 2H), 10.05 (s, 1H).

Preparation of 5,15-bis(4-bromophenyl)-10,20-diphenylporphyrin (6). Compound **3** (2.22 g; 10 mmol) and 4-bromobenzaldehyde (1.85 g; 10 mmol) were dissolved in argon degassed CH₂Cl₂ (500 mL) in a 1000mL two-necked round-bottom flask. The mixture was evacuated and purged with argon three times and the reaction was initiated by the addition of trifluoroacetic acid (0.45 μL; 3.4 mmol). To minimize the amount of side products the reaction flask was fully covered with aluminum foil to protect the content from sunlight. After stirring for 24 h at room temperature, DDQ (2.72 g; 12 mmol) was added and the reaction mixture was further stirred for 1 h. The reaction was quenched by the addition of Et₃N (0.84 mL; 3.4 mmol). The resulting mixture was washed with NaCl solution and the organic fraction was dried over MgSO₄. The product was purified by flash chromatography on silica gel column using CH₂Cl₂ as an eluent.

Yield: 690 mg, 18 %.

¹H NMR (CDCl₃): δ -2.81 (s, 2H); 7.77 (d, 6 H, ³J_{HH} = 7.2 Hz); 7.90 (d, 4 H, ³J_{HH} = 8.0 Hz); 8.08 (d, 4 H, ³J_{HH} = 8.4 Hz); 8.22 (d, 4 H, ³J_{HH} = 6.0 Hz); 8.85 (dt, 8 H).

Table S1. Elemental analysis of CMPs (theoretically expected values based on the structures presented in Figure 1 are in the brackets).

Sample	C / wt %	H / wt %	N / wt %	Pd / wt %
3D-TPP	76.09 (88.03)	3.79 (4.71)	5.14 (7.27)	1.55 (0.00)
3D-PdTPP	72.09 (77.53)	3.07 (3.94)	5.18 (6.40)	11.35 (12.16)
3D-DPP	79.80 (86.38)	3.74 (4.56)	7.52 (9.06)	1.53 (0.00)
2D-TPP	77.07 (88.16)	3.84 (4.97)	5.31 (7.34)	2.50 (0.00)
2D-PdTPP	68.76 (77.55)	2.67 (3.72)	4.99 (6.46)	11.45 (12.27)

Scheme S1. Synthetic procedures of CMP precursors.

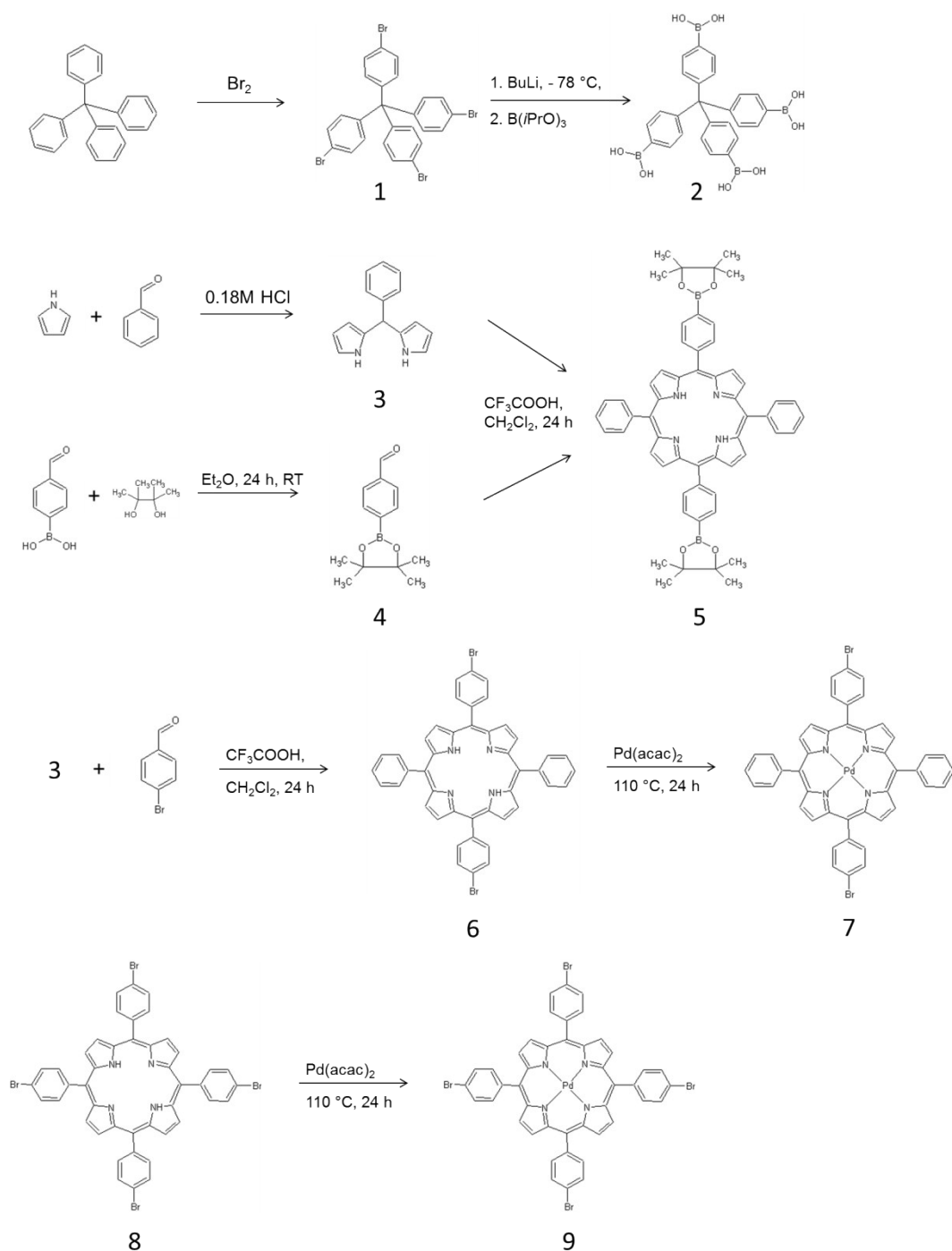


Figure S1. ^{13}C MAS-NMR spectra of CMPs.

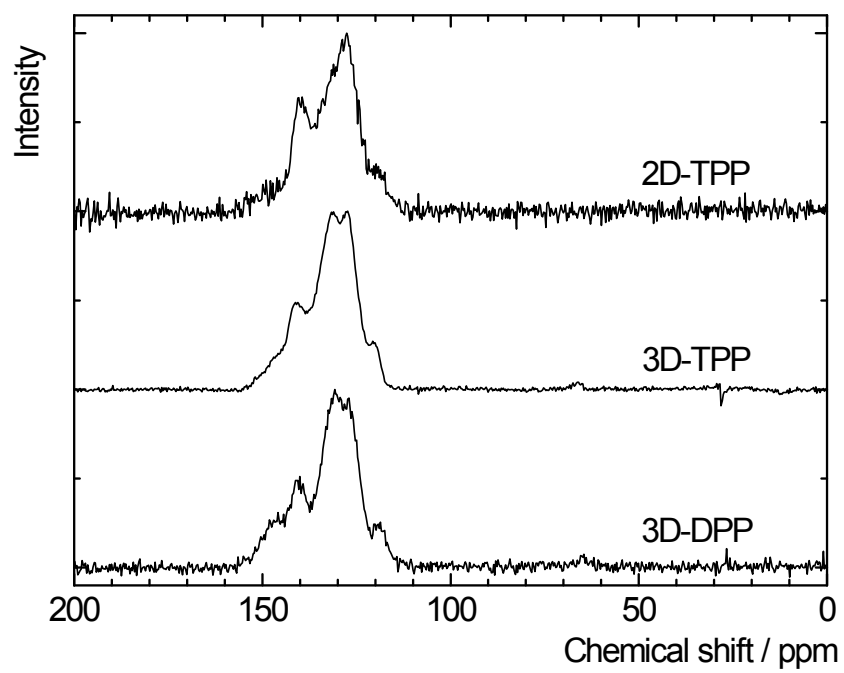


Figure S2. FTIR of CMPs.

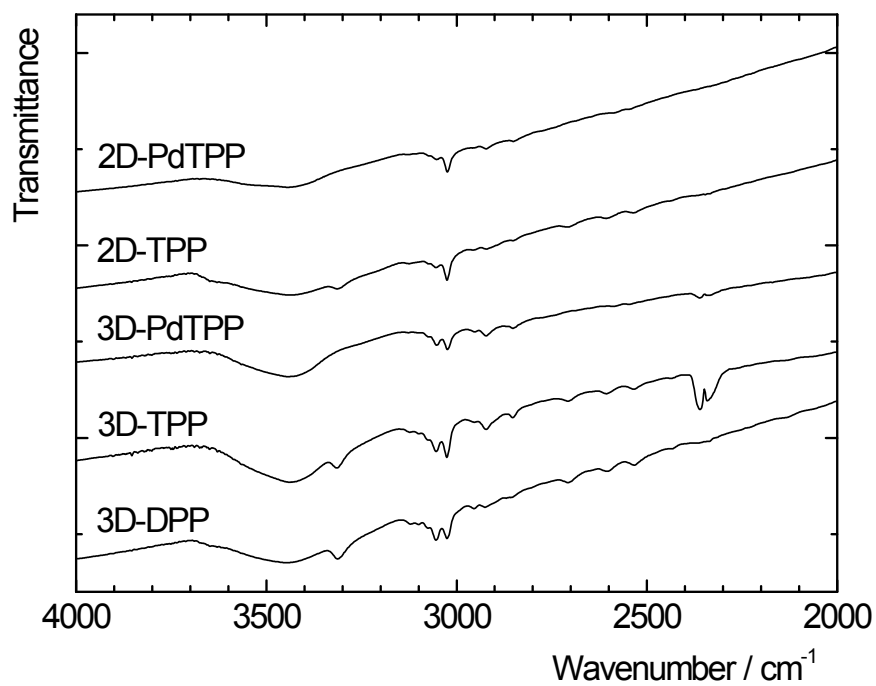
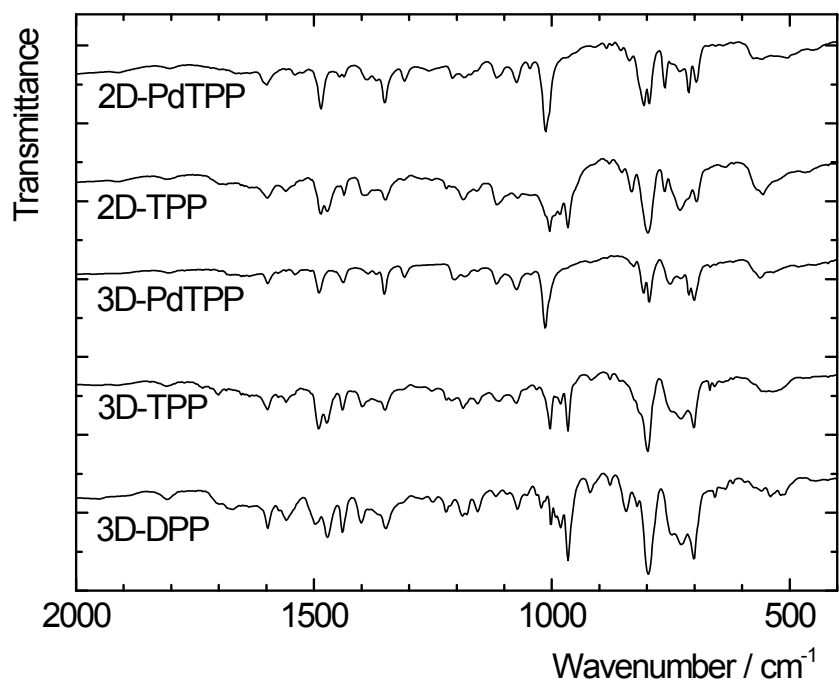


Figure S3. TGA/DTA curves and the evolution of gases for 3D-TPP.

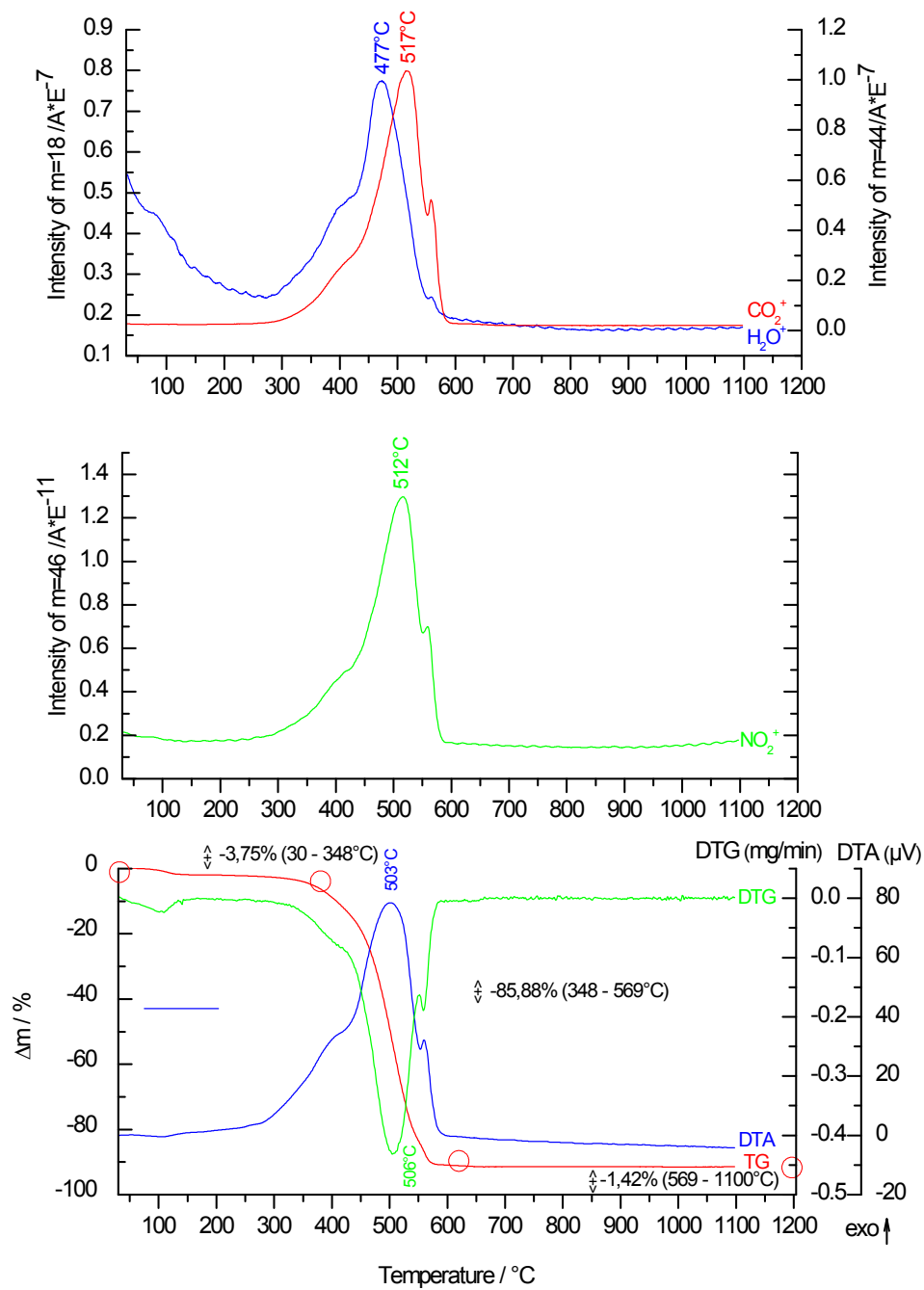


Figure S4. TGA/DTA curves and the evolution of gases for 3D-DPP.

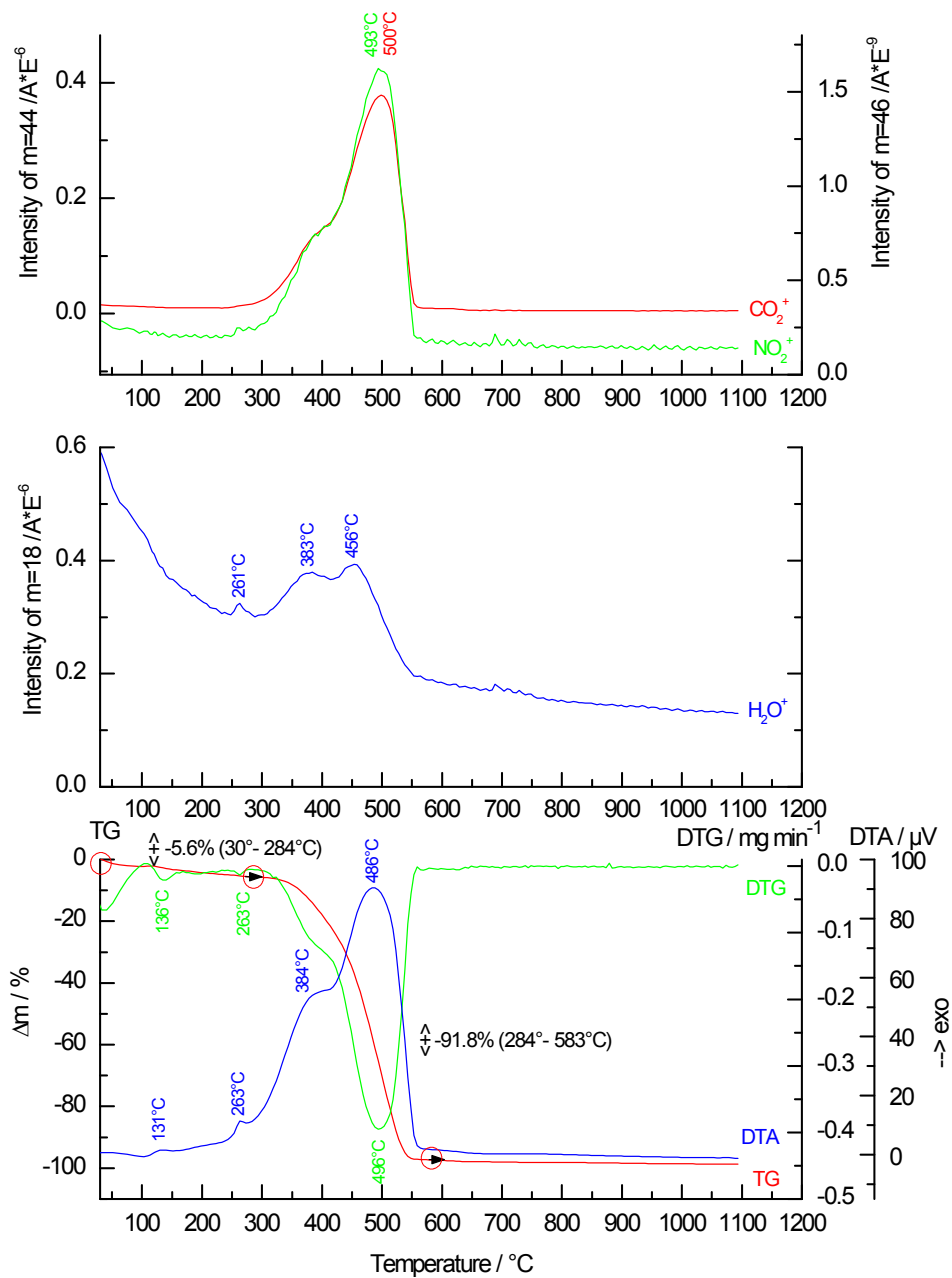


Figure S5. TGA/DTA curves and the evolution of gases for 2D-TPP.

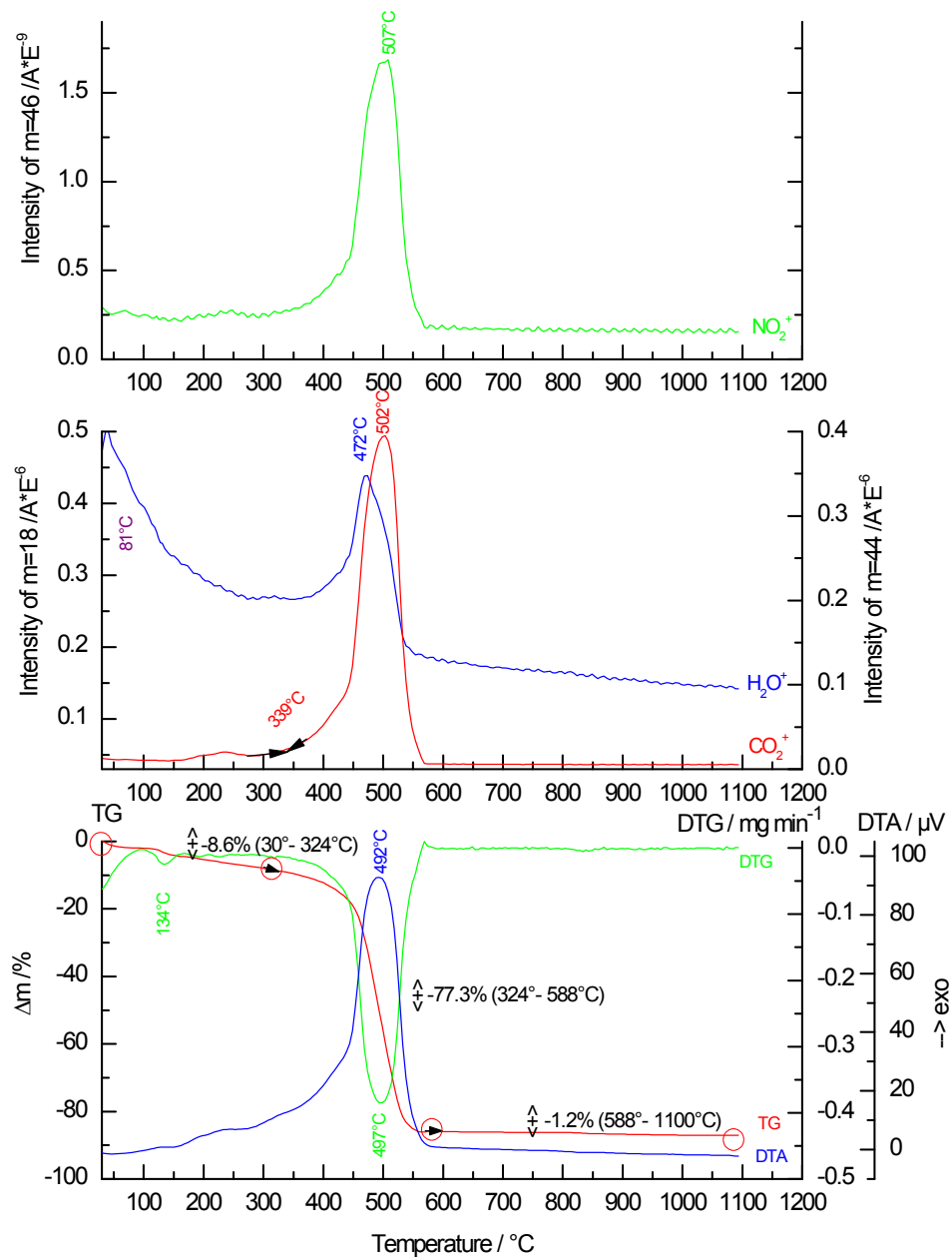


Figure S6. TGA/DTA curves and the evolution of gases for 3D-PdTPP.

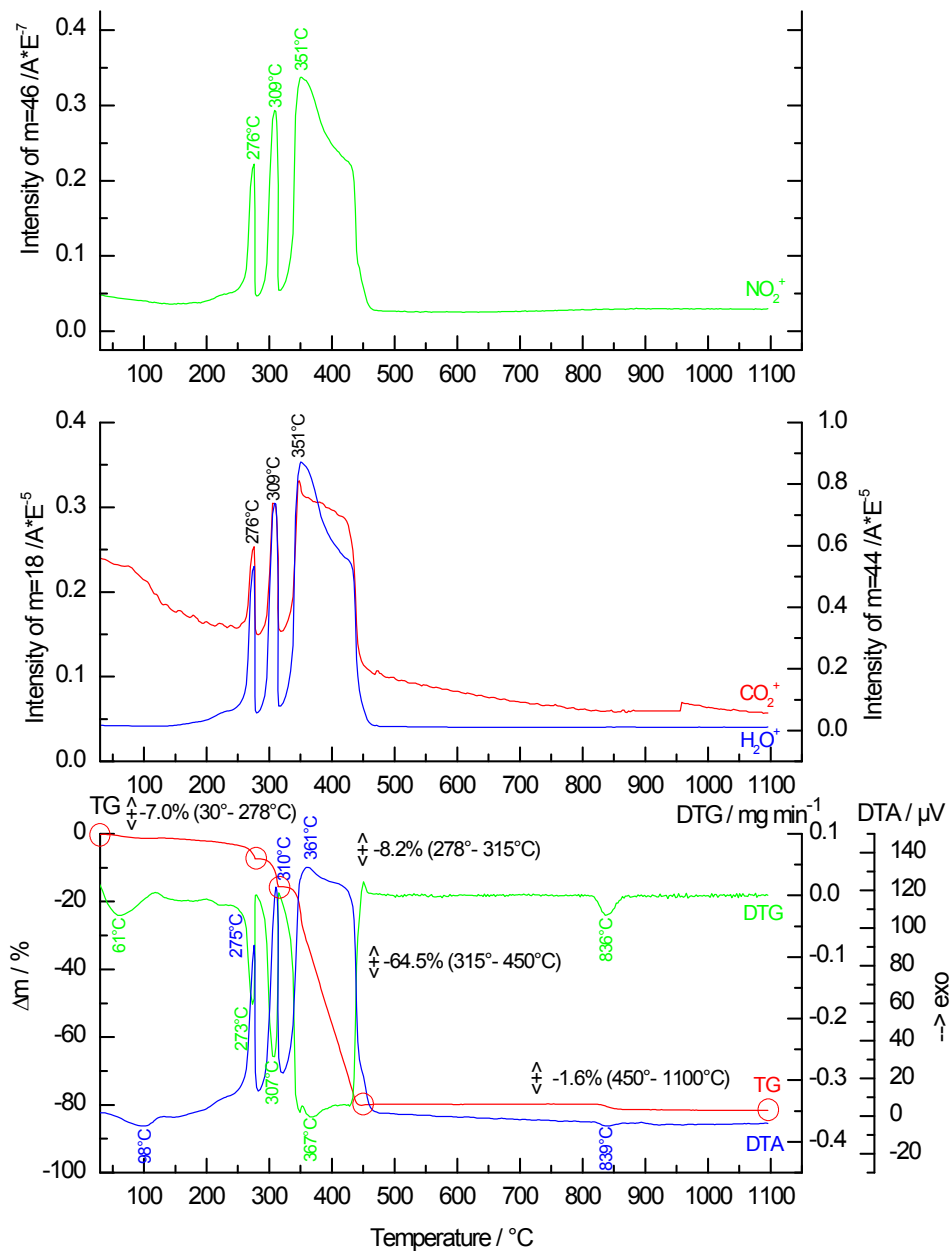


Figure S7. TGA/DTA curves and the evolution of gases for 2D-PdTPP.

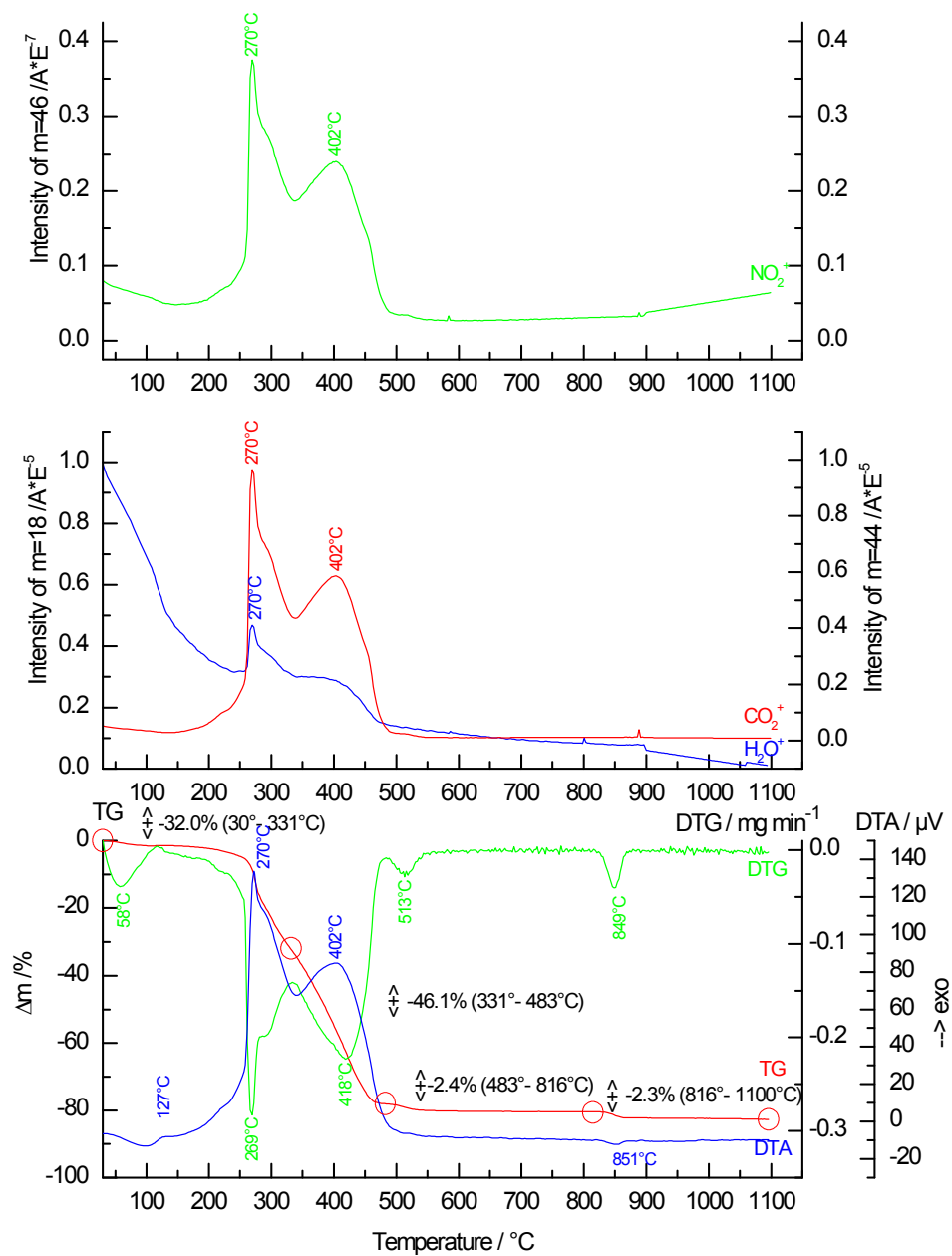


Figure S8. Adsorption isotherms of nitrogen at 77 K for 2D-TPP, 3D-TPP, and 3D-DPP.

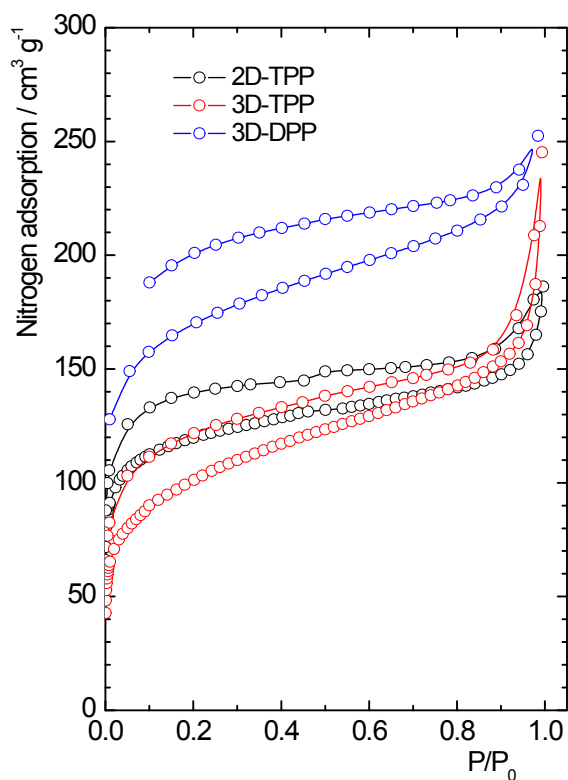


Figure S9. NLDFT pore size distribution calculated from the nitrogen adsorption isotherms presented in Figure S8.

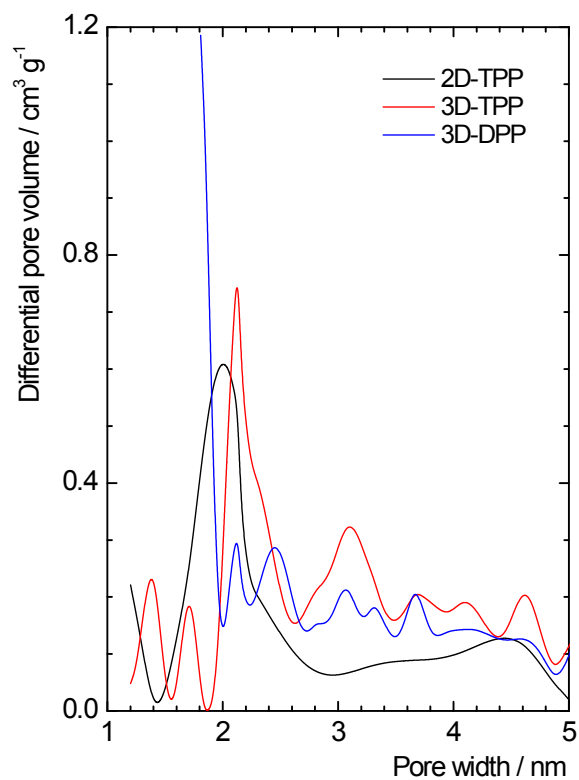


Figure S10. Normalized absorption spectra of CMPs in acetonitrile dispersions.

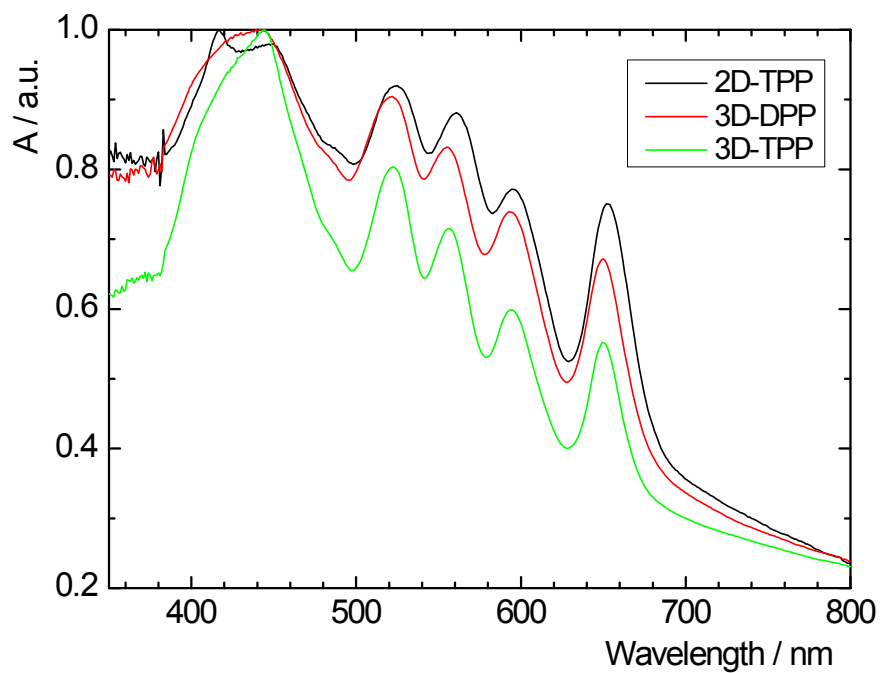


Figure S11. Normalized absorption spectra of 2D-PdTPP and 3D-PdTPP in acetonitrile dispersions.

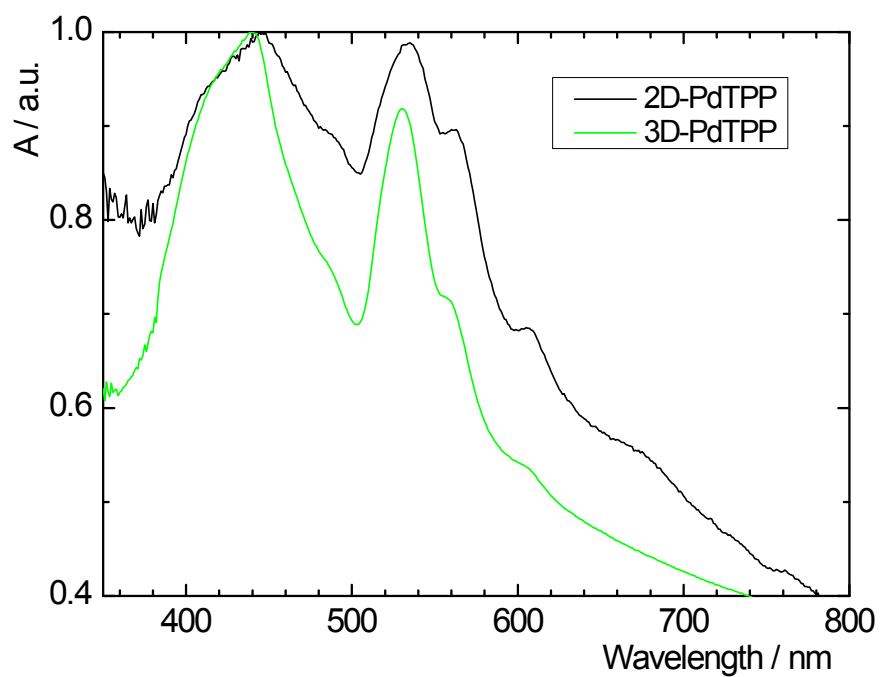


Figure S12. Luminescence emission spectra of 2D-PdTPP dispersions in acetonitrile in the absence of oxygen (a) or saturated by air (b). The excitation wavelength was 440 nm.

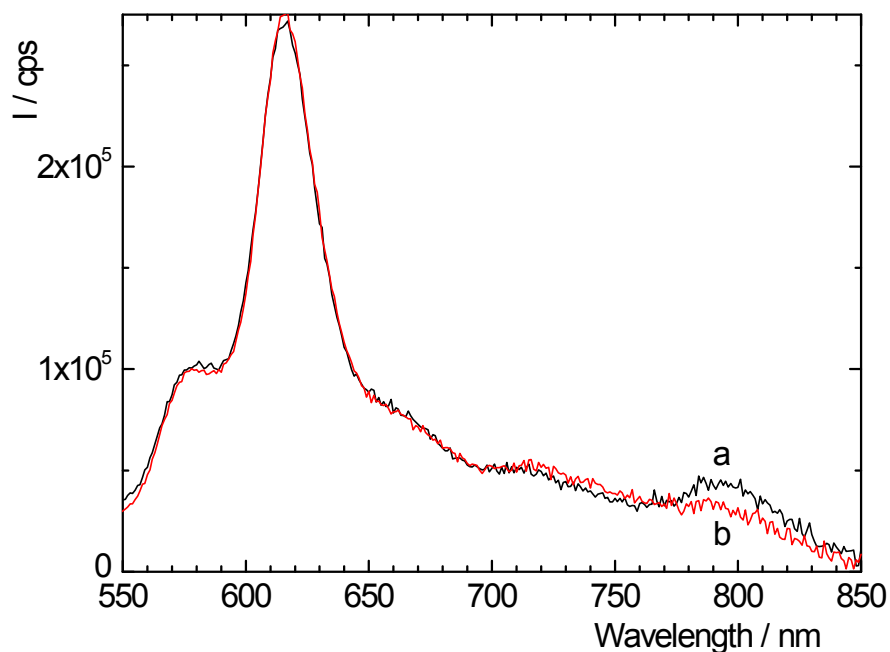


Figure S13. Luminescence emission spectra of photosensitized $O_2(^1\Delta_g)$ produced by 2D-PdTPP (a) and 3D-PdTPP (b) in air atmosphere. The excitation wavelength was 530 nm.

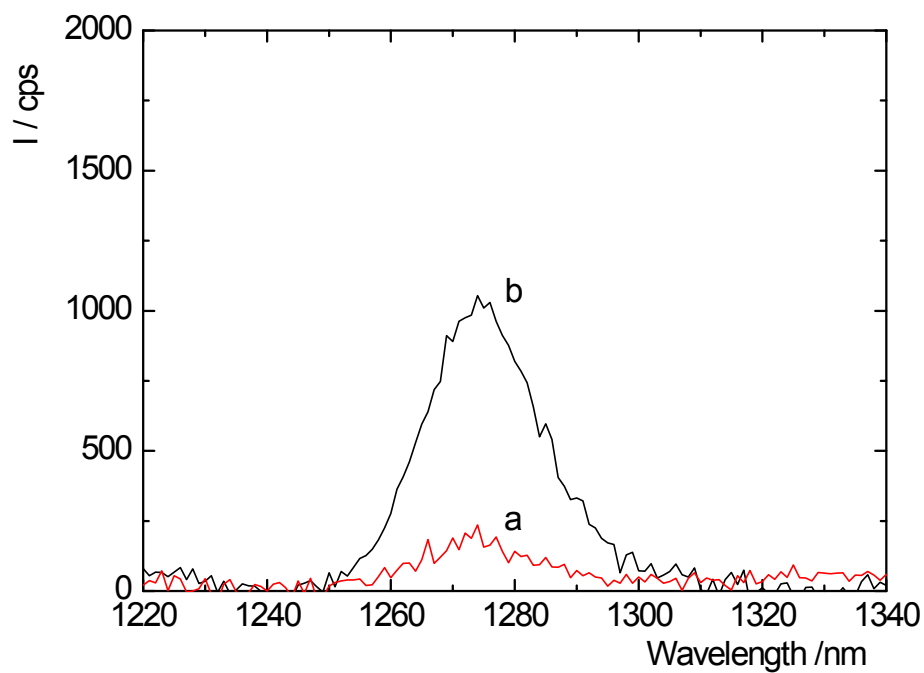


Figure S14. Luminescence emission spectra of photosensitized $O_2(^1\Delta_g)$ produced in acetonitrile dispersions of 2D-PdTPP in oxygen (a), air (b), and argon atmosphere (c) upon excitation at 420 nm.

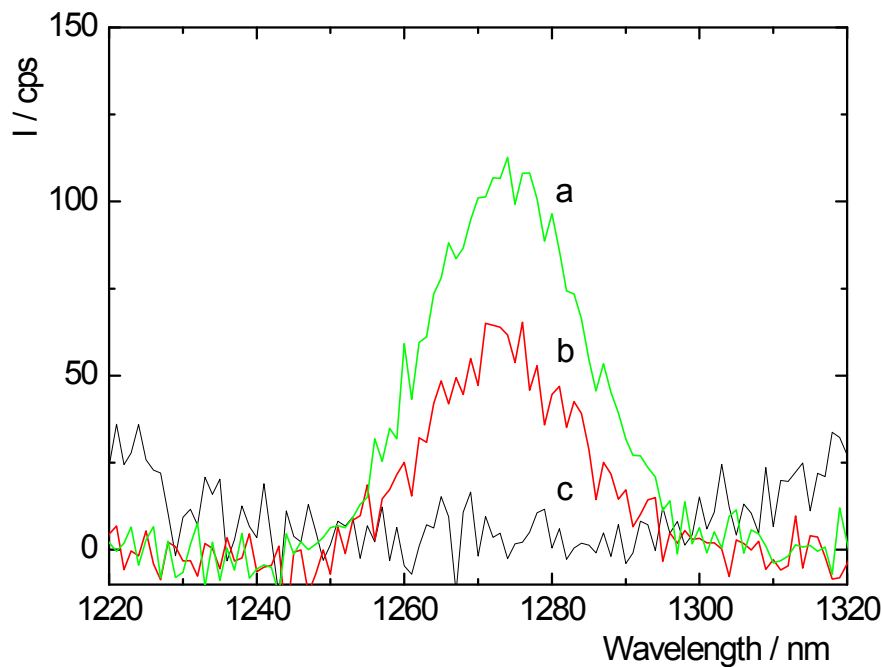


Figure S15. Luminescence emission spectra of photosensitized $O_2(^1\Delta_g)$ produced in acetonitrile dispersions of 3D-TPP in oxygen (a), air (b), and argon atmosphere (c) upon excitation at 420 nm.

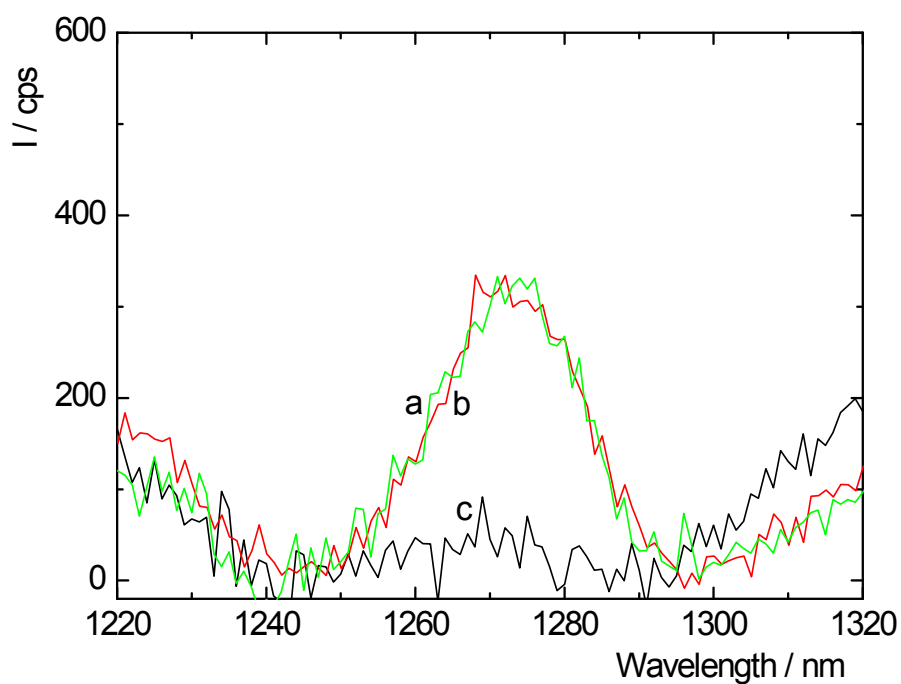


Figure S16. Luminescence emission spectra of photosensitized $O_2(^1\Delta_g)$ produced in acetonitrile dispersions of 3D-DPP in oxygen (a), air (b), and argon atmosphere (c) upon excitation at 420 nm.

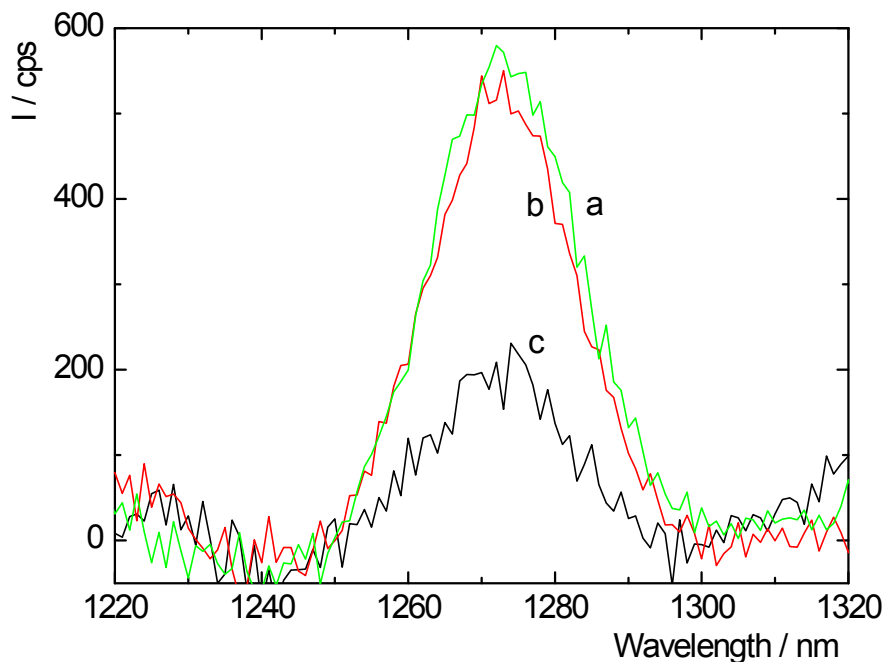
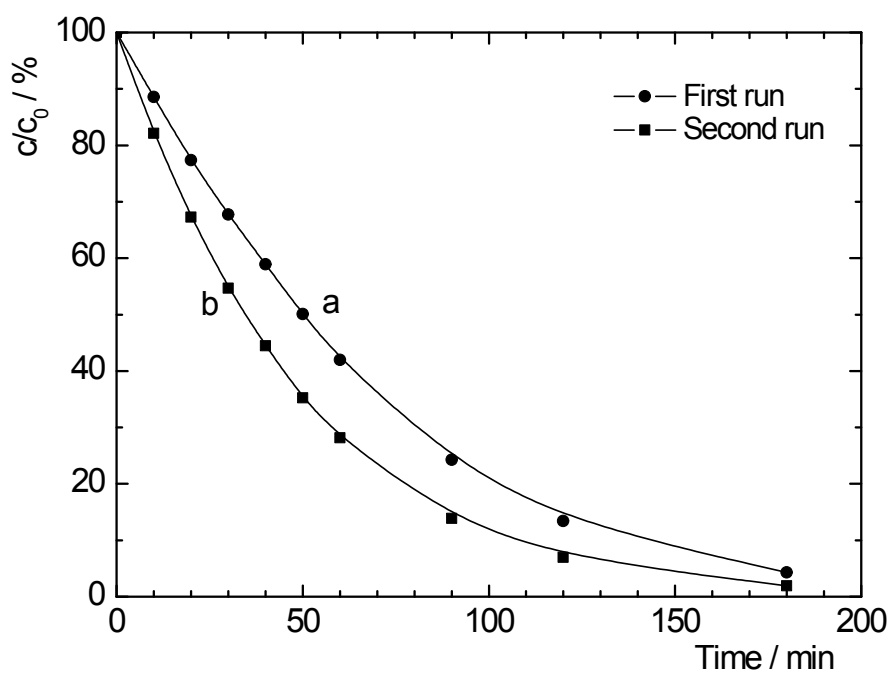


Figure S17. Reaction of photosensitized $O_2(^1\Delta_g)$ produced by 3D-PdTPP dispersions in acetonitrile with 9,10-diphenylanthracene: first (a) and second (b) run.



References

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