

Electronic Supplementary Information (ESI)

**Copper phthalocyanine-based CMPs with
various internal structures and functionalities**

Xuesong Ding and Bao-Hang Han*

*CAS Key Laboratory of Nanosystem and Hierarchical Fabrication,
National Center for Nanoscience and Technology, Beijing 100190, China*

Tel: +86 10 8254 5576. Email: hanbh@nanoctr.cn

Contents

Section A. Materials, synthesis procedures and analysis methods

Section B. Thermal gravimetric analysis

Section C. FT-IR spectral profiles

Section D. FE-SEM images

Section E. HR-TEM images

Section F. PXRD patterns

Section G. Porosity properties: BET plots

Section H. Absorption spectra

Section I. Corresponding data of singlet oxygen generation

Section

J.

References

A. Materials, synthetic procedures, and analysis methods

Materials. Anhydrous *N,N*-dimethylacetamide (DMAc, 99.0%) and chloroform were purchased from Kanto Chemicals. Anhydrous acetone (99.5%) and tetrahydrofuran (THF) were purchased from Wako Chemicals. 4,4'-Biphenyldialdehyde (BPDA) and benzaldehyde were purchased from TCI. 2,5-Dimethoxyterephthalaldehyde (DMTA), anhydrous *N,N*-dimethylformamide (DMF, 99.8%), and 1,3-diphenylisobenzofuran (DPBF) were purchased from Aldrich. Copper tetraaminophthalocyanine ($\text{CuPc}(\text{NH}_2)_4$),^{S1} 2,5-dihydroxyterephthalaldehyde (DHTA),^{S2} 1,3,5-triformylphloroglucinol (TFA),^{S3} 1,3,5-tris(4-formylphenyl)benzene (TFPB),^{S4} 1,3,5-tris(4-formylbiphenyl)benzene (TFBPB),^{S4} tris(4-formylbiphenyl)amine (TFBPA),^{S4} were prepared according to reported methods. $\text{CuPc}(\text{Ph-C=N})_4$ was synthesized by the reaction of $\text{CuPc}(\text{NH}_2)_4$ and benzaldehyde through the method in ref. S5.

Synthesis of CuPc-DHTA-CMP. A DMAc (4.0 mL) solution of $\text{CuPc}(\text{NH}_2)_4$ (44.4 mg, 0.07 mmol) and DHTA (23.3 mg, 0.14 mmol) was degassed in a Pyrex tube (10 mL) by three freeze–pump–thaw cycles. The tube was sealed off and heated at 150 °C for 72 h. After cooling to room temperature, the precipitate was collected by centrifugation, washed with THF, chloroform, and acetone for several times, extracted by Soxhlet with THF for 24 h, and dried at 120 °C under vacuum overnight to give the product as dark green powder in 82% isolated yield. Elemental analysis: for $\text{C}_{48}\text{N}_{12}\text{H}_{24}\text{O}_4\text{Cu}$, calculated: C, 64.32; H, 2.70; N, 18.75%. Found: C, 59.86; H, 3.48; N, 18.42%.

Synthesis of CuPc-DMTA-CMP. A DMAc (4.0 mL) solution of $\text{CuPc}(\text{NH}_2)_4$ (44.4

mg, 0.07 mmol) and DMTA (27.5 mg, 0.14 mmol) was degassed in a Pyrex tube (10 mL) by three freeze–pump–thaw cycles. The tube was sealed off and heated at 150 °C for 72 h. After cooling to room temperature, the precipitate was collected by centrifugation, washed with THF, chloroform, and acetone for several times, extracted by Soxhlet with THF for 24 h, and dried at 120 °C under vacuum overnight to give the product as dark green powder in 79% isolated yield. Elemental analysis: for $C_{52}N_{12}H_{32}O_4Cu$, calculated: C, 65.58; H, 3.39; N, 17.65%. Found: C, 60.72; H, 4.46; N, 17.36%.

Synthesis of CuPc-BPDA-CMP. A DMAc (4.0 mL) solution of CuPc(NH₂)₄ (44.4 mg, 0.07 mmol) and BPDA (29.4 mg, 0.14 mmol) was degassed in a Pyrex tube (10 mL) by three freeze–pump–thaw cycles. The tube was sealed off and heated at 150 °C for 72 h. After cooling to room temperature, the precipitate was collected by centrifugation, washed with THF, chloroform, and acetone for several times, extracted by Soxhlet with THF for 24 h, and dried at 120 °C under vacuum overnight to give the product as dark green powder in 75% isolated yield. Elemental analysis: for $C_{60}N_{12}H_{32}Cu$, calculated: C, 73.20; H, 3.28; N, 17.07%. Found: C, 68.48; H, 4.18; N, 16.88%.

Synthesis of CuPc-TFA-CMP. A DMAc (4.0 mL) solution of CuPc(NH₂)₄ (38.2 mg, 0.06 mmol) and TFA (16.7 mg, 0.08 mmol) was degassed in a Pyrex tube (10 mL) by three freeze–pump–thaw cycles. The tube was sealed off and heated at 150 °C for 72 h. After cooling to room temperature, the precipitate was collected by centrifugation, washed with THF, chloroform, and acetone for several times, extracted by Soxhlet

with THF for 24 h, and dried at 120 °C under vacuum overnight to give the product as dark green powder in 77% isolated yield. Elemental analysis: for $C_{44}N_{12}H_{20}O_4Cu$, calculated: C, 62.60; H, 2.39; N, 19.91%. Found: C, 57.46; H, 3.24; N, 19.62%.

Synthesis of CuPc-TFPB-CMP. A DMAc (4.0 mL) solution of $CuPc(NH_2)_4$ (38.2 mg, 0.06 mmol) and TFPB (31.2 mg, 0.08 mmol) was degassed in a Pyrex tube (10 mL) by three freeze–pump–thaw cycles. The tube was sealed off and heated at 150 °C for 72 h. After cooling to room temperature, the precipitate was collected by centrifugation, washed with THF, chloroform, and acetone for several times, extracted by Soxhlet with THF for 24 h, and dried at 120 °C under vacuum overnight to give the product as dark green powder in 80% isolated yield. Elemental analysis: for $C_{68}N_{12}H_{36}Cu$, calculated: C, 75.30; H, 3.35; N, 15.50%. Found: C, 70.54; H, 4.22; N, 15.18%.

Synthesis of CuPc-TFBPB-CMP. A DMAc (4.0 mL) solution of $CuPc(NH_2)_4$ (38.2 mg, 0.06 mmol) and TFBPB (55.6 mg, 0.08 mmol) was degassed in a Pyrex tube (10 mL) by three freeze–pump–thaw cycles. The tube was sealed off and heated at 150 °C for 72 h. After cooling to room temperature, the precipitate was collected by centrifugation, washed with THF, chloroform, and acetone for several times, extracted by Soxhlet with THF for 24 h, and dried at 120 °C under vacuum overnight to give the product as dark green powder in 77% isolated yield. Elemental analysis: for $C_{92}N_{12}H_{52}Cu$, calculated: C, 79.55; H, 3.77; N, 12.10%. Found: C, 75.30; H, 4.82; N, 11.92%.

Synthesis of CuPc-TFBPA-CMP. A DMAc (4.0 mL) solution of $CuPc(NH_2)_4$ (38.2

mg, 0.06 mmol) and TFBPA (44.6 mg, 0.08 mmol) was degassed in a Pyrex tube (10 mL) by three freeze–pump–thaw cycles. The tube was sealed off and heated at 150 °C for 72 h. After cooling to room temperature, the precipitate was collected by centrifugation, washed with THF, chloroform, and acetone for several times, extracted by Soxhlet with THF for 24 h, and dried at 120 °C under vacuum overnight to give the product as dark green powder in 79% isolated yield. Elemental analysis: for $C_{84}N_{13.33}H_{48}Cu$, calculated: C, 77.16; H, 3.70; N, 14.28%. Found: C, 73.68; H, 4.32; N, 14.16%.

Analysis methods. Fourier transform infrared (FT-IR) spectra were recorded on a JASCO model FT-IR-6100 infrared spectrometer. Elemental analysis was performed on a Yanako model CHN CORDER MT-6 elemental analyzer. Thermogravimetric analysis (TGA) measurements were performed on a Mettler-Toledo model TGA/SDTA851e under nitrogen, by heating to 1000 °C at a rate of 10 °C min⁻¹. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from $2\theta = 1.5^\circ$ up to 60° with 0.02° increment. Field-emission scanning electron microscopy (FE-SEM) images were performed on a JEOL model JSM-6700 operating at an accelerating voltage of 5.0 kV. The samples were prepared by drop-casting a THF suspension onto mica substrate and then coated with gold. High-resolution transmission electron microscopy (HR-TEM) images were obtained on a JEOL model JEM-3200 microscopy. The sample was prepared by drop-casting a THF suspension of the CuPc-CMPs samples onto a carbon-coated copper grid. Nitrogen sorption isotherms

were measured at 77 K with a Micromeritics Instrument Corporation model 3Flex surface characterization analyzer. Ultraviolet–visible (UV-Vis) diffuse reflectance spectra (Kubelka-Munk spectrum) were recorded on a JASCO model V-670 spectrometer equipped with integration sphere model IJN-727.

B. Thermal gravimetric analysis

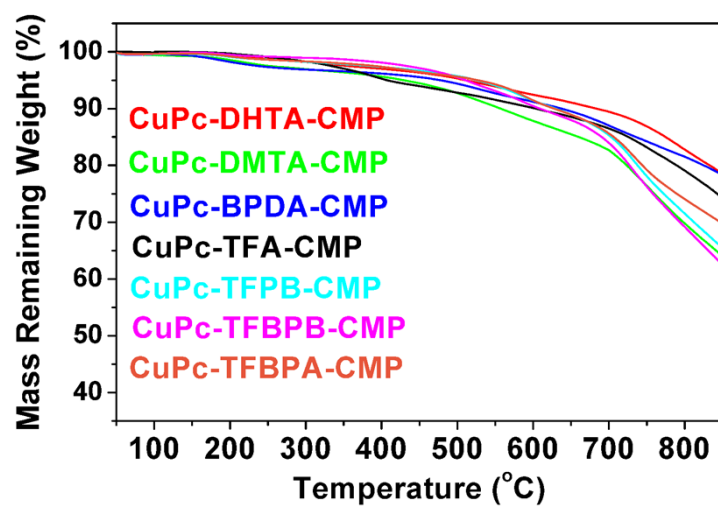


Fig. S1 TGA curves of CuPc-CMPs.

C. FT-IR spectral profiles

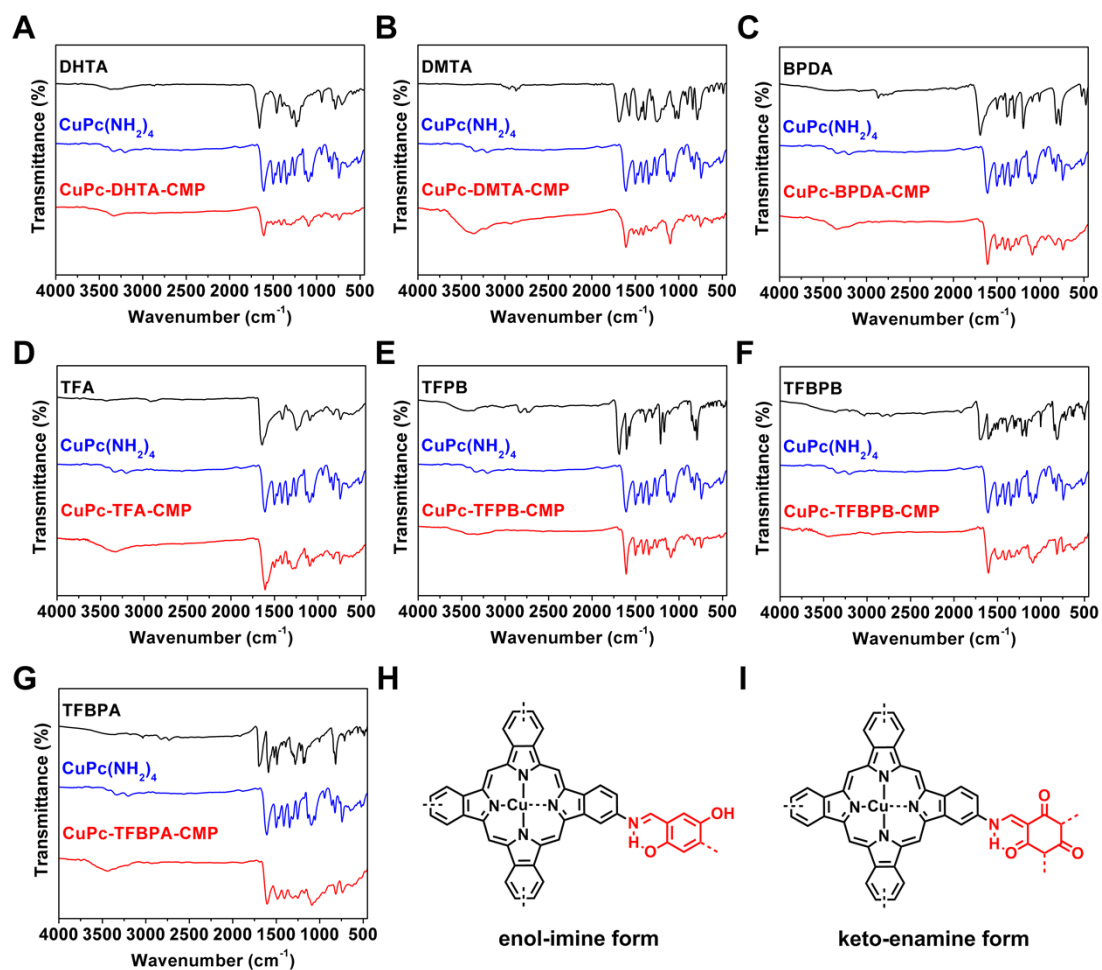


Fig. S2 (A)–(G) FT-IR spectra of CuPc-CMPs compared with their monomers. (H) and (I) Structures of enol-imine form and keto-enamine form in CuPc-CMPs.

D. FE-SEM images

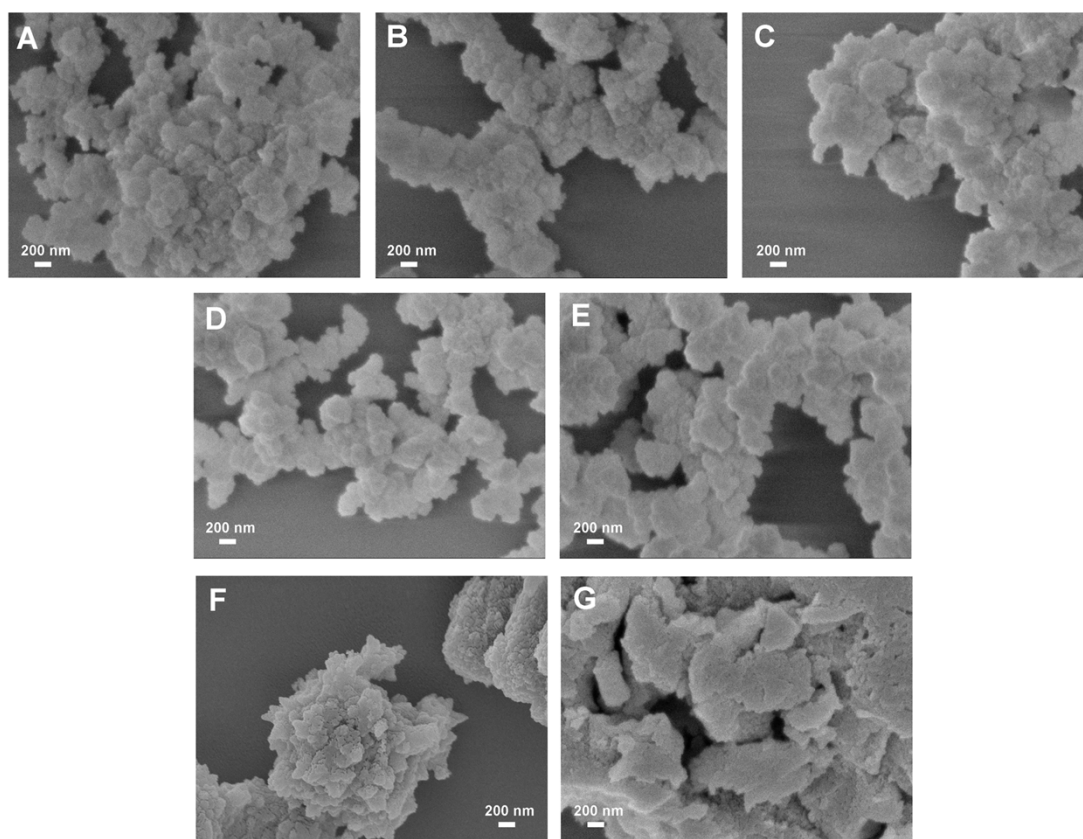


Fig. S3 FE-SEM images of (A) CuPc-DHTA-CMP, (B) CuPc-DMTA-CMP, (C) CuPc-BPDA-CMP, (D) CuPc-TFA-CMP, (E) CuPc-TFPB-CMP, (F) CuPc-TFBPB-CMP, and (G) CuPc-TFBPA-CMP.

E. HR-TEM images

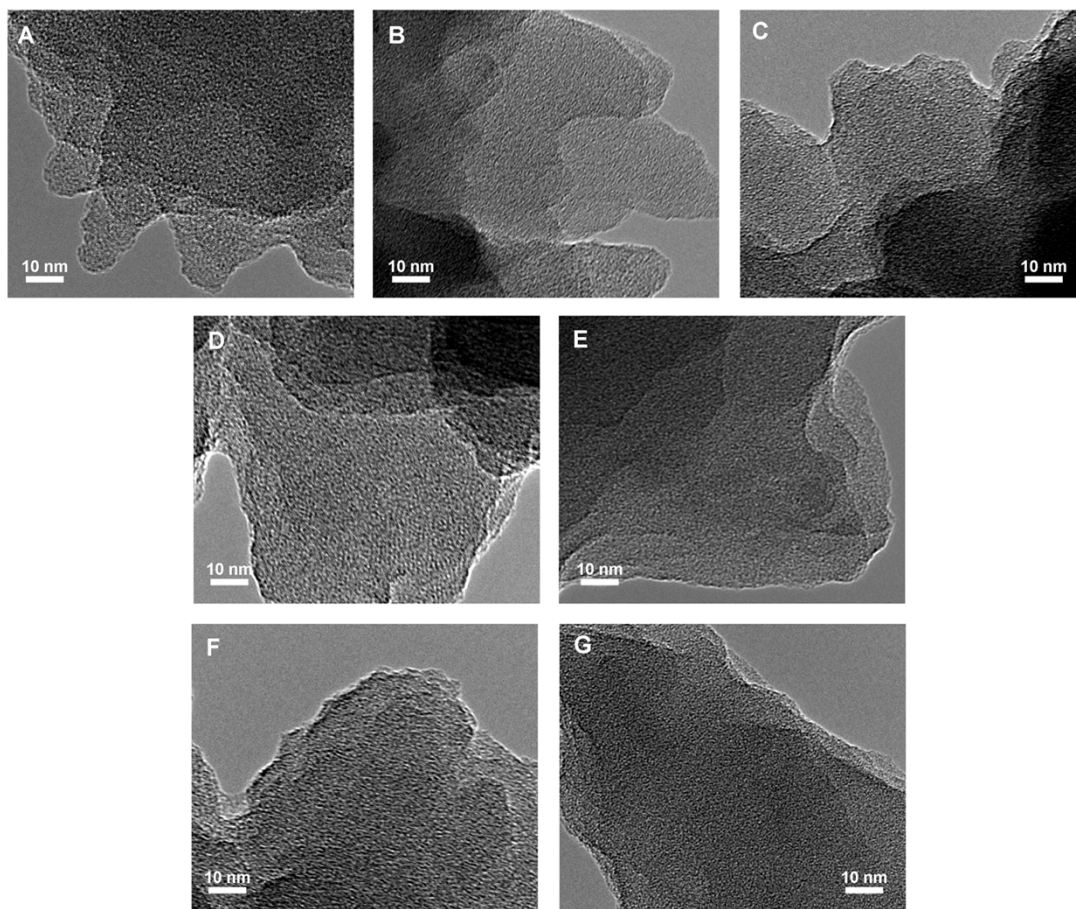


Fig. S4 HR-TEM images of (A) CuPc-DHTA-CMP, (B) CuPc-DMTA-CMP, (C) CuPc-BPDA-CMP, (D) CuPc-TFA-CMP, (E) CuPc-TFPB-CMP, (F) CuPc-TFBPB-CMP, and (G) CuPc-TFBPA-CMP.

F. PXRD patterns

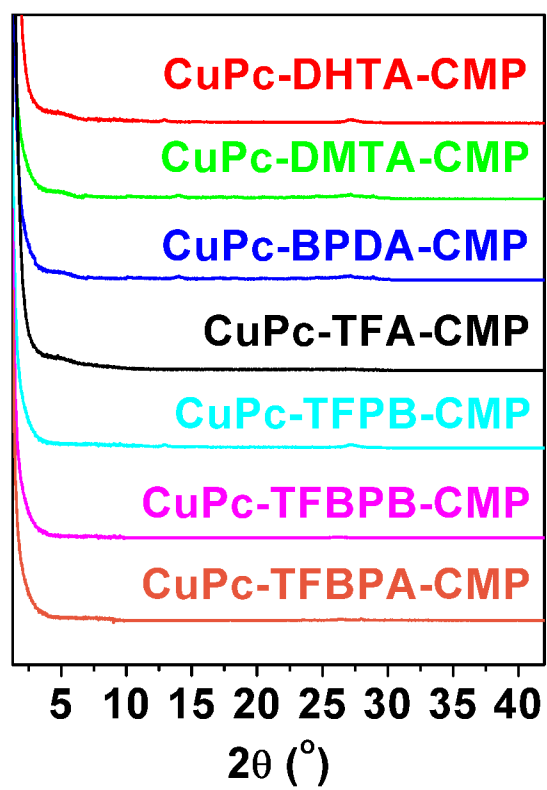


Fig. S5 PXRD patterns of CuPc-CMPs.

G. Porosity properties: BET plots

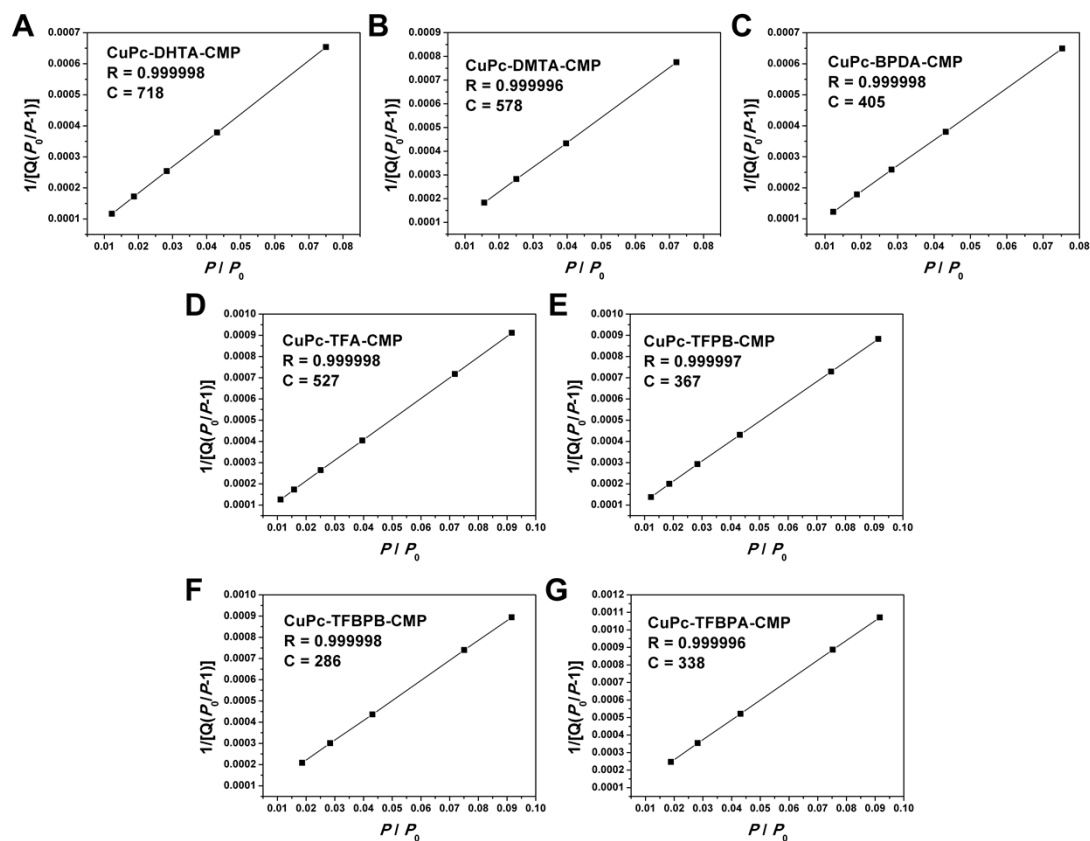


Fig. S6 BET plots of (A) CuPc-DHTA-CMP, (B) CuPc-DMTA-CMP, (C) CuPc-BPDA-CMP, (D) CuPc-TFA-CMP, (E) CuPc-TFPB-CMP, (F) CuPc-TFBPB-CMP, and (G) CuPc-TFBPA-CMP from nitrogen adsorption data.

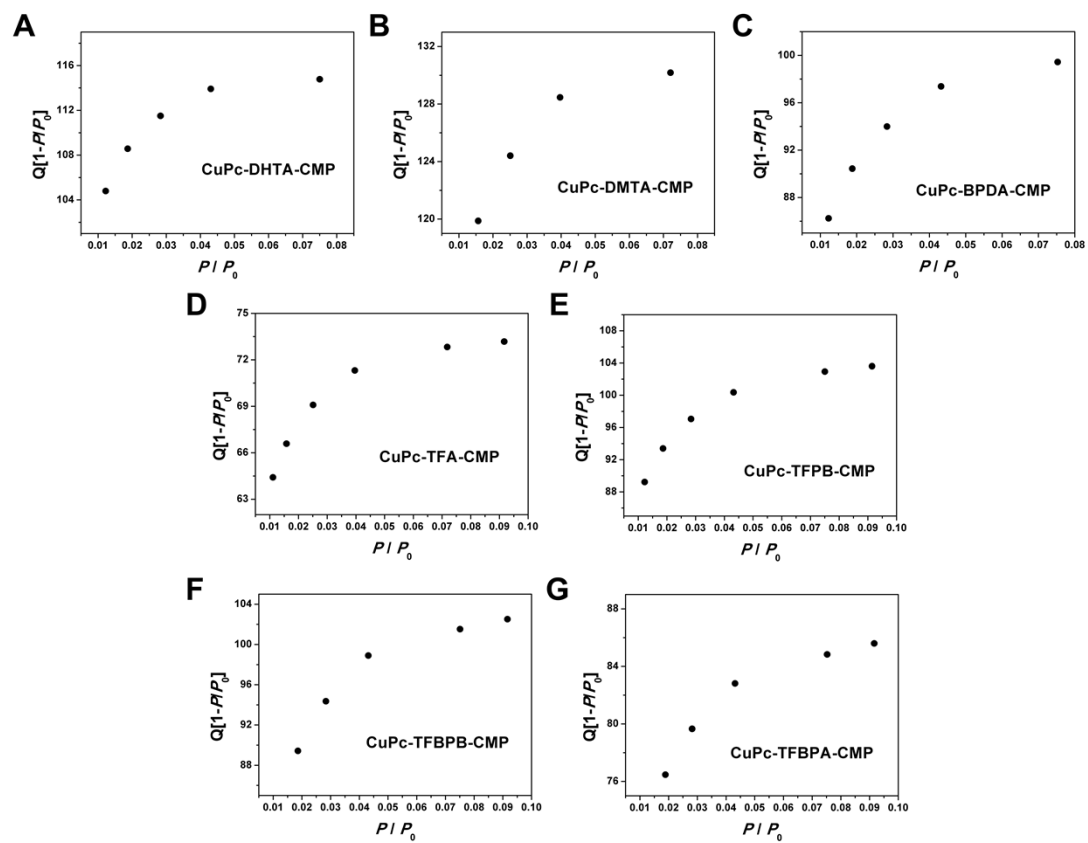


Fig. S7 Rouquerol plots of (A) CuPc-DHTA-CMP, (B) CuPc-DMTA-CMP, (C) CuPc-BPDA-CMP, (D) CuPc-TFA-CMP, (E) CuPc-TFPB-CMP, (F) CuPc-TFBPB-CMP, and (G) CuPc-TFBPA-CMP from nitrogen adsorption data.

Table S1. Porosity properties of CuPc-CMPs.

CuPc-CMPs	S_{BET}^a ($\text{m}^2 \text{g}^{-1}$)	S_{micro}^b ($\text{m}^2 \text{g}^{-1}$)	V_{micro}^c ($\text{cm}^3 \text{g}^{-1}$)	V_{total}^d ($\text{cm}^3 \text{g}^{-1}$)	D_{pore}^e (nm)
CuPc-DHTA-CMP	510	390	0.16	0.68	1.49
CuPc-DMTA-CMP	410	320	0.13	0.72	1.49
CuPc-BPDA-CMP	520	420	0.17	0.73	1.56
CuPc-TFA-CMP	450	290	0.12	0.56	1.52
CuPc-TFPB-CMP	460	280	0.11	0.92	1.49
CuPc-TFBPB-CMP	410	360	0.13	0.37	1.42
CuPc-TFBPA-CMP	380	240	0.10	0.73	1.38

^a Specific surface area calculated from the nitrogen adsorption isotherm using the BET method in the relative pressure (P/P_0) range from 0.01 to 0.10.

^b Micropore surface area calculated from the nitrogen adsorption isotherm using the t -plot method.

^c Micropore volume calculated from the nitrogen adsorption isotherm using the t -plot method.

^d Total pore volume at $P/P_0 = 0.99$.

^e Pore size calculated from the nitrogen adsorption isotherm using NLDFT method. Model is N_2 at 77 K on carbon (slit/cylindr. pores, QSDFT adsorption branch).

H. Absorption spectra

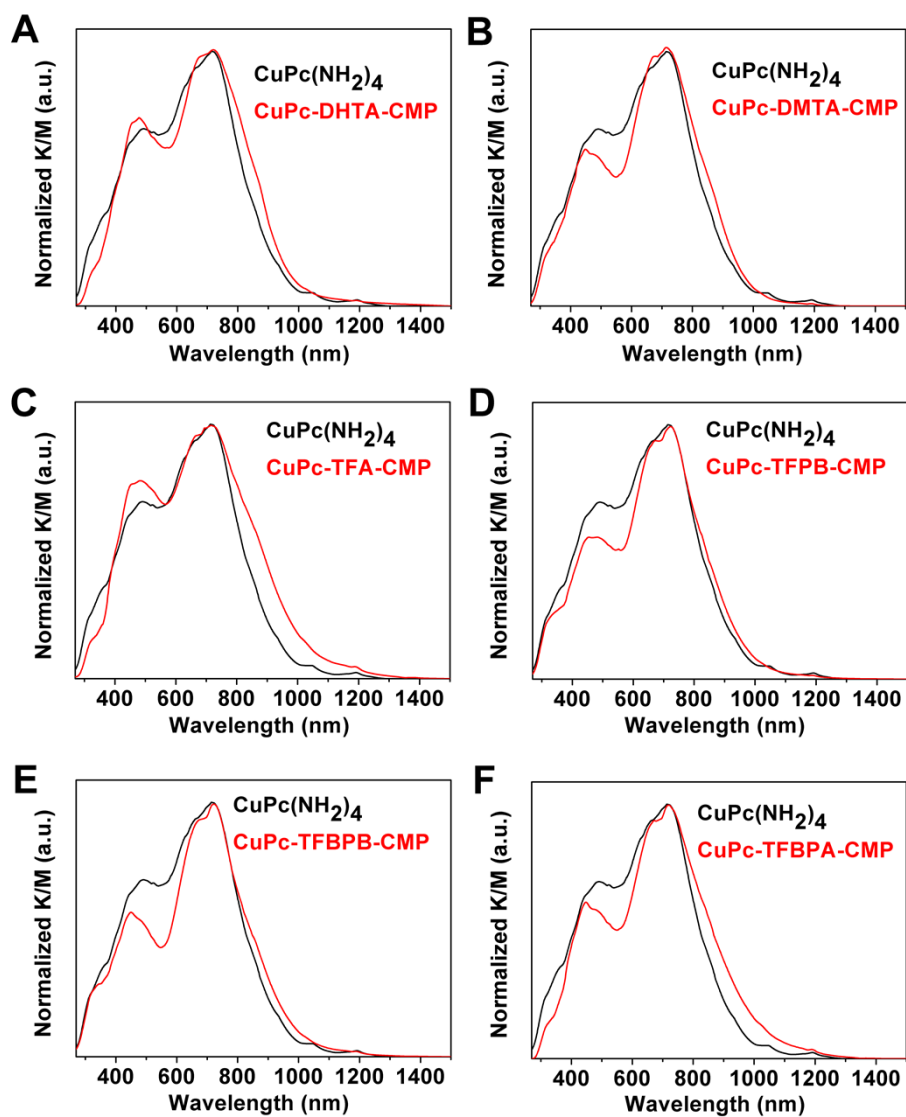


Fig. S8 Absorption spectra of CuPc-CMPs compared with their monomers.

I. Corresponding data of singlet oxygen generation

For detecting of singlet oxygen generation, an oxygen-saturated DMF solution (2.5 mL) of DPBF (50 μM) in the presence of the monomeric $\text{CuPc}(\text{Ph-C}=\text{N})_4$ (0.1 μmol) or CuPc-CMPs (0.1 mg, 0.1 μmol for CuPc unit) in a quartz cell (branched with a 10-mL flask) connected to an oxygen balloon was irradiated with a visible light at 700 nm (bandpass filter) from a Xenon lamp of Asahi Spectra model Max 301. The time-dependent electronic absorption spectra were recorded on a JASCO model V-670 spectrometer.

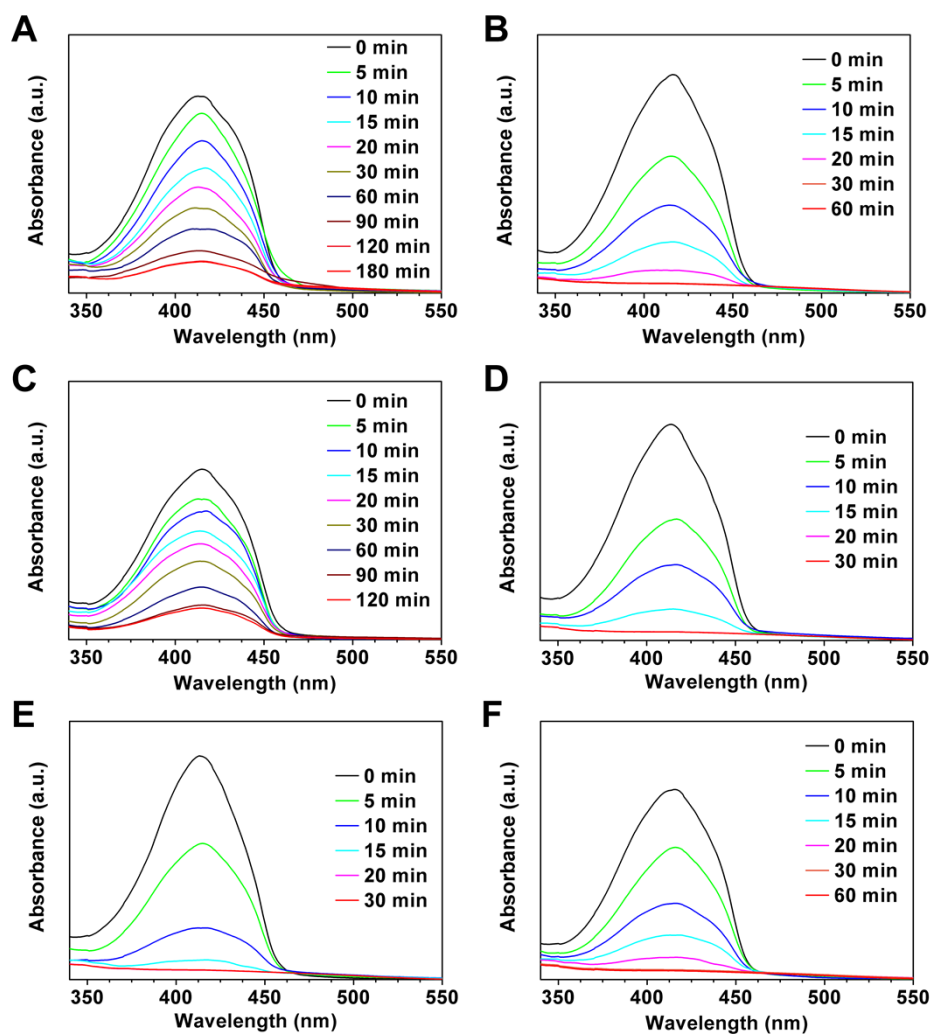


Fig. S9 Time-dependent absorption spectra of DPBF (in DMF) upon irradiation at 700 nm in the presence of (A) CuPc-DHTA-CMP, (B) CuPc-DMTA-CMP, (C) CuPc-TFA-CMP, (D) CuPc-TFPB-CMP, (E) CuPc-TFBPB-CMP, and (F) CuPc-TFBPA-CMP, respectively.

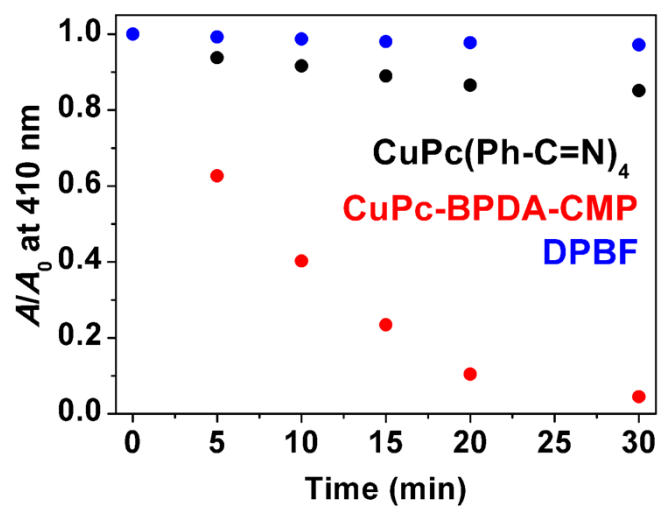


Fig. S10 Comparison of decay rate of DPBF (blue), and in the presence of CuPc-BPDA-CMP (red) and CuPc(Ph-C=N)₄ (black), respectively.

Table S2. Average decay rate of DPBF in 15 min in the presence of CuPc(Ph-C=N)₄ or CuPc-CMPs.

Samples	Average Rate (% min ⁻¹) ^a
CuPc(Ph-C=N) ₄	0.74 ^b
CuPc-DHTA-CMP	2.44
CuPc-DMTA-CMP	5.10
CuPc-BPDA-CMP	5.61
CuPc-TFA-CMP	2.42
CuPc-TFPB-CMP	5.70
CuPc-TFBPB-CMP	6.08
CuPc-TFBPA-CMP	5.11

^a Average decay rate of DPBF in 15 min in the presence of the samples.

^b Ref. S5.

J. References

- S1. B. N. Achar, G. M. Fohlen, J. A. Parker and J. Keshavayya, *Polyhedron*, 1987, **6**, 1463–1467.
- S2. (a) A. Palmgren, A. Thorarensen and J. Bäckvall, *J. Org. Chem.*, 1998, **63**, 3764–3768; (b) N. Kuhnert, G. M. Rossignolo and A. L. Periago, *Org. Biomol. Chem.*, 2003, **1**, 1157–1170; (c) T. Kretz, J. W. Bats, H. W. Lerner and T. Wagner, *Z. Naturforsch.*, 2007, **62b**, 66–74.
- S3. B. Lukose, A. Kuc, T. Heine, *Chem. Eur. J.*, 2011, **17**, 2388–2392.
- S4. Y.-C. Zhao, T. Wang, L.-M. Zhang, Y. Cui and B.-H. Han, *ACS Appl. Mater. Interfaces*, 2012, **4**, 6975–6981.
- S5. X. Ding and B.-H. Han, *Angew. Chem., Int. Ed.*, 2015, **54**, 6536–6539.