Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Core–shell conjugated microporous polymers: a new strategy for exploring color-tunable and -controllable light emissions

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Section A. Materials and methods

1,2,4,5-tetrabromobenzene, benzene-1,4-diboronic acid, *N*, *N*-dimethylformamide, and tetrakis(triphenylphosphine)-palladium(0) were purchased from Aldrich Chemicals. 1,1,2,2-tetraphenylethene was purchased from TCI. Methanol, acetone, tetrahydrofunan, and dichloromethane were purchased from Wako Chemicals. Chloroform was purchased from Kanto Co. Tetrakis(4-bromophenyl)ethene (TBTPE) and 1,2-bis(4-bromophenyl)-1,2-diphenylethene (DBPE) were synthesized according to the reported method.[S1,S2]

Fourier transform Infrared (FT-IR) spectra were recorded on a JASCO model FT-IR-6100 infrared spectrometer. UV-Vis-IR diffuse reflectance spectra (Kubelka-Munk spectrum) were recorded on a JASCO model V-670 spectrometer equipped with integration sphere model IJN-727. Photoluminescence spectra were recorded on a JASCO model FP-6600 spectrofluorometer. The absolute quantum yield was determined by standard procedure with an integral sphere JASCO model ILF-533 mounted on the FP-6600 spectrofluorometer. Time-resolved fluorescence spectroscopy of solid samples was recorded on Hamamatsu compact fluorescence lifetime spectrometer Quantaurus–Tau model C11367-11. 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 CMP samples onto a copper grid. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from $2\theta = 1.5°$ up to 60° with 0.02° increment.

Nitrogen sorption isotherms were measured at 77 K with a Bel Japan Inc. model BELSORP-mini II analyzer. Before measurement, the samples were degassed in vacuum at 150 °C for more than 10 h. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas and pore volume, the Saito-Foley (SF) method was applied for the estimation of pore size and pore size distribution.

Section B. Synthetic procedures

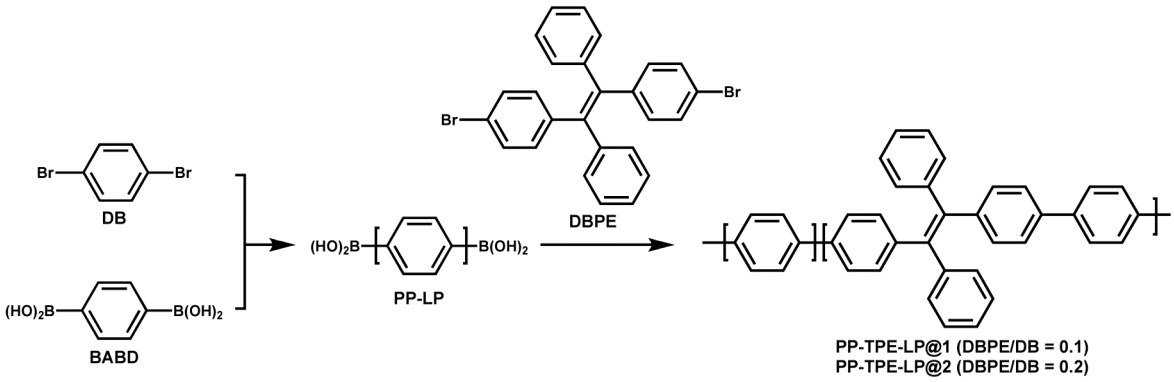
PP_C-CMP. A mixture of 1,2,4,5-tetrabromobenzene (TBB) (50 mg, 0.127 mmol), and benzene-1,4-diboronic acid (BDBA) (63.1 mg, 0.381 mmol) in DMF (12 mL) was degassed by three freeze–pump–thaw cycles. To the mixture was added an aqueous solution of K_2CO_3 (1.0 M, 1.0 mL) and $Pd(PPh_3)_4$ (12.0 mg, 10.4 μmol). The mixture was degassed by three freeze–pump–thaw cycles, and purged with argon, and stirred at 90 °C for 20 h. The precipitate was filtered, washed with water, methanol, acetone, tetrahydrofuran, and dichloromethane to remove any unreacted monomers or catalyst residues. Further purification was carried out by Soxhlet extraction with water, methanol, and tetrahydrofuran for 24 h, respectively, to give PP_C-CMP as grey solid in 87% isolation yield. Elemental analysis (%) Found: C 82.04, H 5.01.

TPE_S-PP_C-CMP@1, TPE_S-PP_C-CMP@2, TPE_S-PP_C-CMP@3, and TPE_S-PP_C-CMP@4. A mixture of TBB (50 mg, 0.127 mmol) and BDBA (63.1 mg, 0.381 mmol) in DMF (12 mL) was degassed by three freeze–pump–thaw cycles. To the mixture was added an aqueous solution of K_2CO_3 (1.0 M, 1.0 mL) and $Pd(PPh_3)_4$ (12.0 mg, 10.4 μmol). The mixture was degassed by three freeze–pump–thaw cycles, purged with Ar, and stirred at 90 °C for 20 h. The mixture was allowed to cool at room temperature, and was added with a mixture of TBTPE/aqueous solution (1 M) of K_2CO_3/$Pd(PPh_3)_4$ (15.9 μmol/0.16 mL/1.59 μmol for TPE_S-PP_C-CMP@1, 25.4 μmol/0.2 mL/2.03 μmol for TPE_S-PP_C-CMP@2, 38.1 μmol/0.3 mL/3.05 μmol for TPE_S-PP_C-CMP@3, 50.8 μmol/0.4 mL/4.06 μmol for TPE_S-PP_C-CMP@4, respectively). The resulting mixture was degassed by three freeze–pump–thaw cycles purged with Ar, and stirred at 120 °C for 3 days. The precipitate was collected by filtration, thoroughly washed with water, dichloromethane, methanol, and tetrahydrofuran, dried under vacuum at 120 °C, and rigorously washed by Soxhlet extractions for 24 h with water, dichloromethane, methanol, and THF, respectively, to give TPE_S-PP_C-CMP@1, TPE_S-PP_C-CMP@2, TPE_S-PP_C-CMP@3, and TPE_S-PP_C-CMP@4, respectively, as gray powders in 81-97% isolation yields. Elemental analysis (%) C 82.30, H 4.75 (TPE_S-PP_C-CMP@1), C 86.01, H 4.91 (TPE_S-PP_C-CMP@2), C 87.36, H 4.94 (TPE_S-PP_C-CMP@3), and C 81.88, H 4.67 (TPE_S-PP_C-CMP@4).

TPE_C-CMP. A mixture of TBTPE (50 mg, 0.077 mmol) and BDBA (38.3 mg, 0.231 mmol) in DMF (12 mL) was degassed by three freeze–pump–thaw cycles. To the mixture was added an aqueous solution of K_2CO_3 (1.0 M, 0.61 mL) and $Pd(PPh_3)_4$ (7.1 mg, 6.16 μmol). The resulting solution was further degassed for three cycles, and purged with argon, and stirred at 90 °C for 20

h. After the mixture was cooled to room temperature, the precipitate was filtered and washed with water, methanol, acetone, tetrahydrofuran, and dichloromethane to remove any unreacted monomers or catalyst residues. Further purification of the polymer was carried out by Soxhlet extraction with water, methanol, and tetrahydrofuran for 24 h, respectively, to give TPE_C-CMP as green powder in 89% isolation yield. Elemental analysis (%) C 75.87, H 4.77.

PP_S-TPE_C-CMP@1, PP_S-TPE_C-CMP@3, and PP_S-TPE_C-CMP@5. A mixture of TBTPE (50 mg, 0.077 mmol) and BDBA (38.3 mg, 0.231 mmol) in DMF (12 mL) was degassed by three freeze–pump–thaw cycles. To the mixture was added an aqueous solution of K_2CO_3 (1.0 M, 0.61 mL) and $Pd(PPh_3)_4$ (7.1 mg, 6.16 μmol). The resulting solution was degassed by three freeze–pump–thaw cycles, purged with argon, and stirred at 90 °C for 20 h. The mixture was allowed to cool at room temperature, and was added with a mixture of TBB/aqueous solution (1 M) of K_2CO_3/$Pd(PPh_3)_4$ (9.62 μmol/0.076 mL/0.77 μmol for PP_S-TPE_C-CMP@1, 19.25 μmol/0.152 mL/1.54 μmol for PP_S-TPE_C-CMP@3, 38.5 μmol/0.304 mL/3.85 μmol for PP_S-TPE_C-CMP@5, respectively). The mixture was degassed by three freeze–pump–thaw cycles, purged with Ar, and stirred at 120 °C for 3 days. The precipitate was collected by filtration, thoroughly washed with water, dichloromethane, and methanol, respectively. The precipitate was rigorously washed by Soxhlet extractions for 24 h with water, dichloromethane, methanol and THF, respectively, and dried under vacuum at 120 °C, to give PP_S-TPE_C-CMP@1, PP_S-TPE_C-CMP@3, and PP_S-TPE_C-CMP@5, respectively, as yellowish green powders in 83-88% isolation yields. Elemental analysis (%) C 83.32, H 4.87 (PP_S-TPE_C-CMP@1), C 86.24, H 5.04 (PP_S-TPE_C-CMP@3), and C 87.39, H 4.99 (PP_S-TPE_C-CMP@5).



Scheme S1. Schematic representation of the synthesis of linear conjugated polymer analogues PP-TPE-LPs by the Suzuki cross-coupling reaction.

PP-LP. A mixture of 1, 4-dibromobenzene (DB) (50 mg, 0.212 mmol) and BDBA (52.7 mg,

0.318 mmol) in DMF (12 mL) was degassed by three freeze–pump–thaw cycles. To the mixture was added an aqueous solution of K_2CO_3 (1.0 M, 0.84 mL) and $Pd(PPh_3)_4$ (9.8 mg, 8.48 μmol). The mixture was degassed by three freeze–pump–thaw cycles, purged with Ar, and stirred at 90 °C for 20 h. The precipitate was collected by filtration, thoroughly washed with water and ethanol, and dried under vacuum at 120 °C, to give PP-LP as gray powder in 82% isolation yield. Elemental analysis (%) C 86.20, H 5.35.

PP-TPE-LP@1 and PP-TPE-LP@2. A mixture of DB (50 mg, 0.212 mmol) and BDBA (52.7 mg, 0.318 mmol) in DMF (12 mL) was degassed by three freeze–pump–thaw cycles. To the mixture was added an aqueous solution of K_2CO_3 (1.0 M, 0.84 mL) and $Pd(PPh_3)_4$ (9.8 mg, 8.48 μmol). The mixture was further degassed by three freeze–pump–thaw cycles, purged with Ar, and stirred at 90 °C for 20 h. The mixture was allowed to cool at room temperature and was added with a mixture of DBPE/aqueous solution (1 M) of K_2CO_3/$Pd(PPh_3)_4$ (21.2 μmol/0.084 mL/1.59 μmol for PP-TPE-LP@1 (DBPE/DB = 0.1), 42.4 μmol/0.168 mL/3.18 μmol for PP-TPE-LP@2 (DBPE/DB = 0.2)). The mixture was degassed by three freeze–pump–thaw cycles, purged with Ar, and stirred at 120 °C for 3 days. The precipitate was collected by filtration, thoroughly washed with water and ethanol, and dried under vacuum at 120 °C, to give PP-TPE-LP@1 and PP-TPE-LP@2, respectively, as gray powders in 67 and 61% isolation yield, respectively. Elemental Analysis (%) C 85.02, H 5.41 (PP-TPE-LP@1), C 84.93, H 5.48 (PP-TPE-LP@2).

Macroscopically linked CMPs. A mixture of PP-CMP with phenyl boronic acid surface (4 mg) and TPE-CMP with phenyl boromide periphery (4 mg) in DMF (10 mL) was degassed by three freeze–pump–thaw cycles. To the mixture was added an aqueous solution of K_2CO_3 (1.0 M, 0.1 mL) and $Pd(PPh_3)_4$ (3.0 mg, 2.6 μmol). The mixture was degassed by three freeze–pump–thaw cycles, and purged with argon, and stirred at 90 °C for 3 days. The precipitate was filtered and washed with water, methanol, acetone, tetrahydrofuran, and dichloromethane. Further purification was carried out by Soxhlet extraction with water, methanol, and tetrahydrofuran for 24 h, respectively, to give the macroscopically linked CMPs quantitatively.

Section C. FT-IR spectral profiles

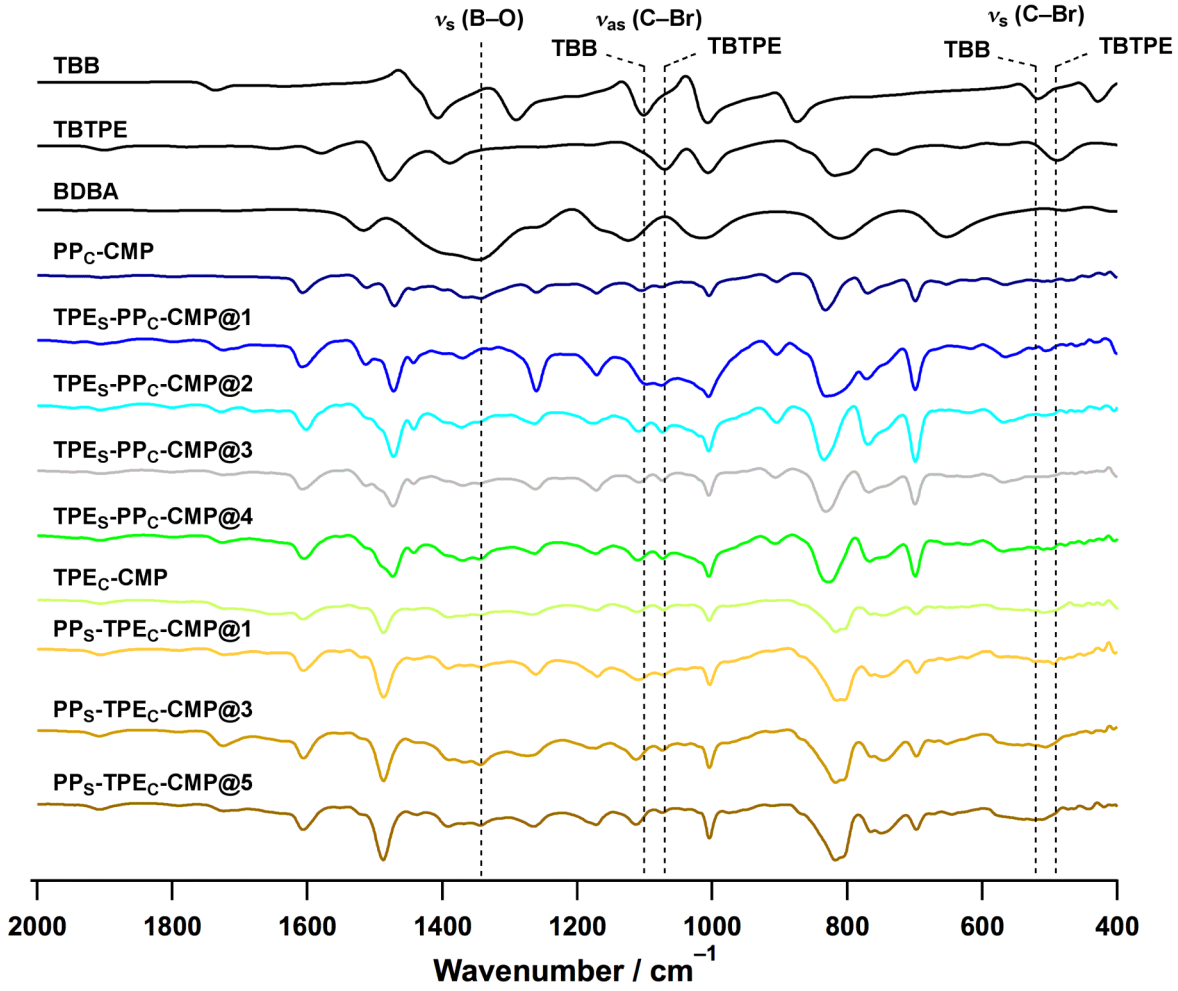


Figure S1. FT-IR spectra of the CMPs. The B–O bonds in the core CMPs disappeared after the growth of the shell CMPs.

Section D. Fluorescence images of macroscopically linked CMPs

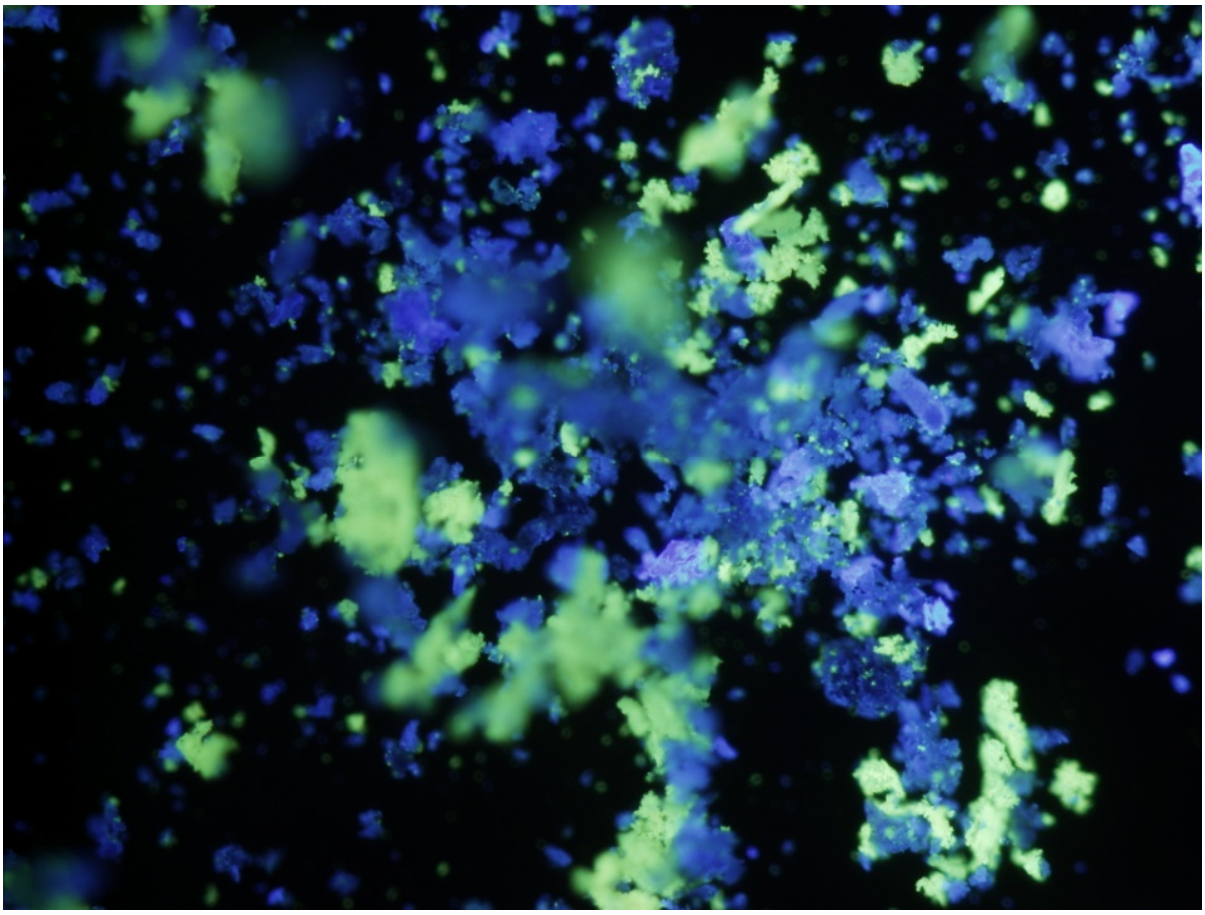


Figure S2. Fluorescence images of macroscopically linked CMPs.

Section E. Powder X-ray diffraction patterns

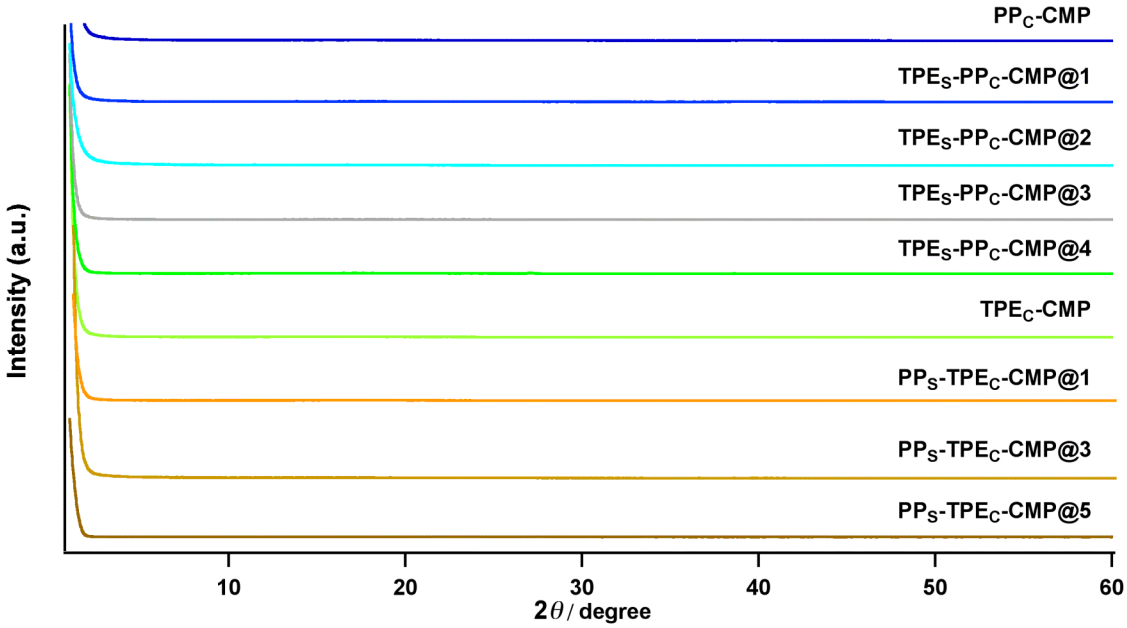


Figure S3. Powder X-ray diffraction profiles of core–shell-structured CMPs.

Section F. Porous structure

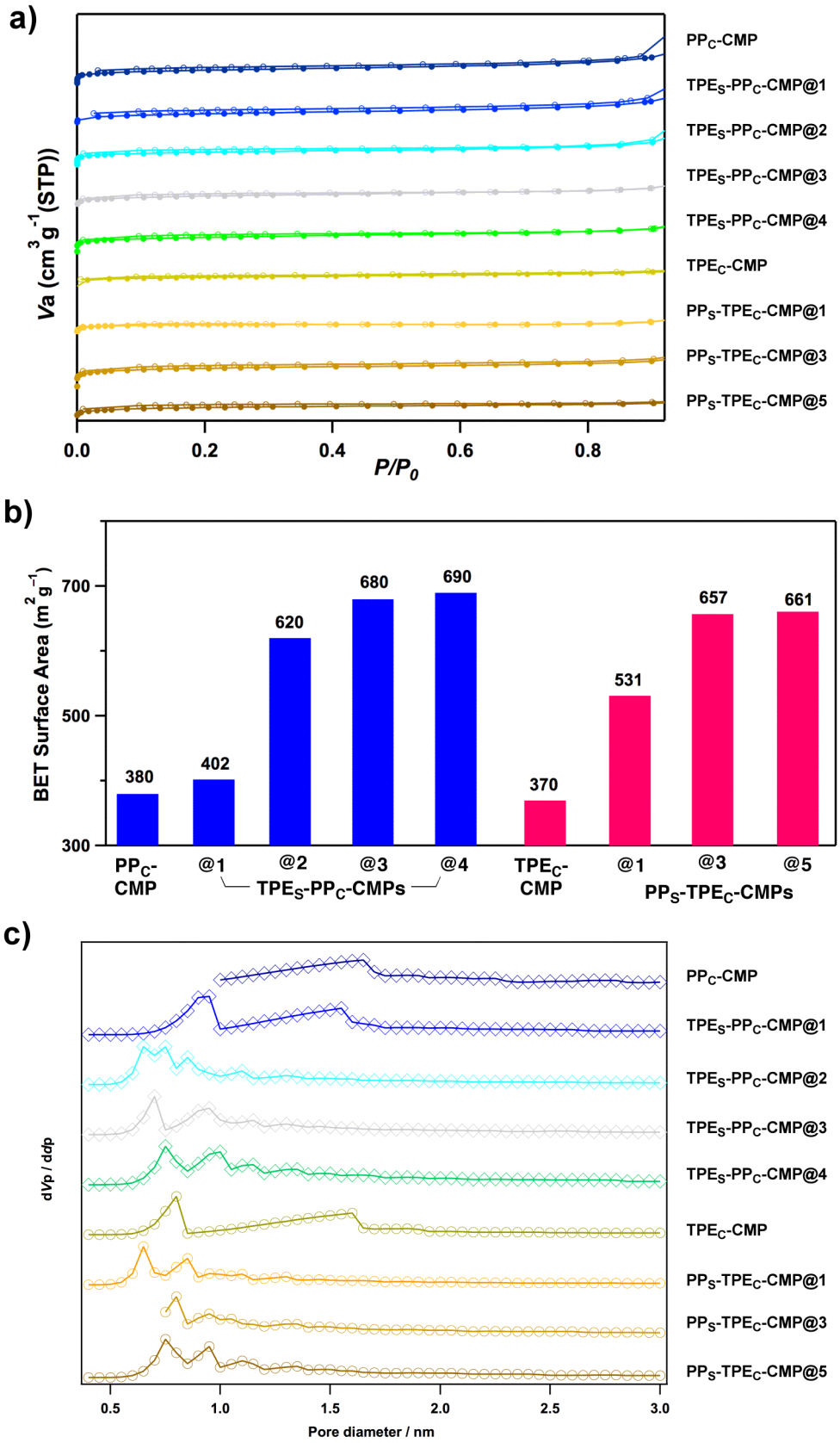


Figure S4. (a) Nitrogen sorption isotherm curves of the CMPs. (b) BET surface areas. (c) Pore size distribution profiles.

Section G. FE-SEM images

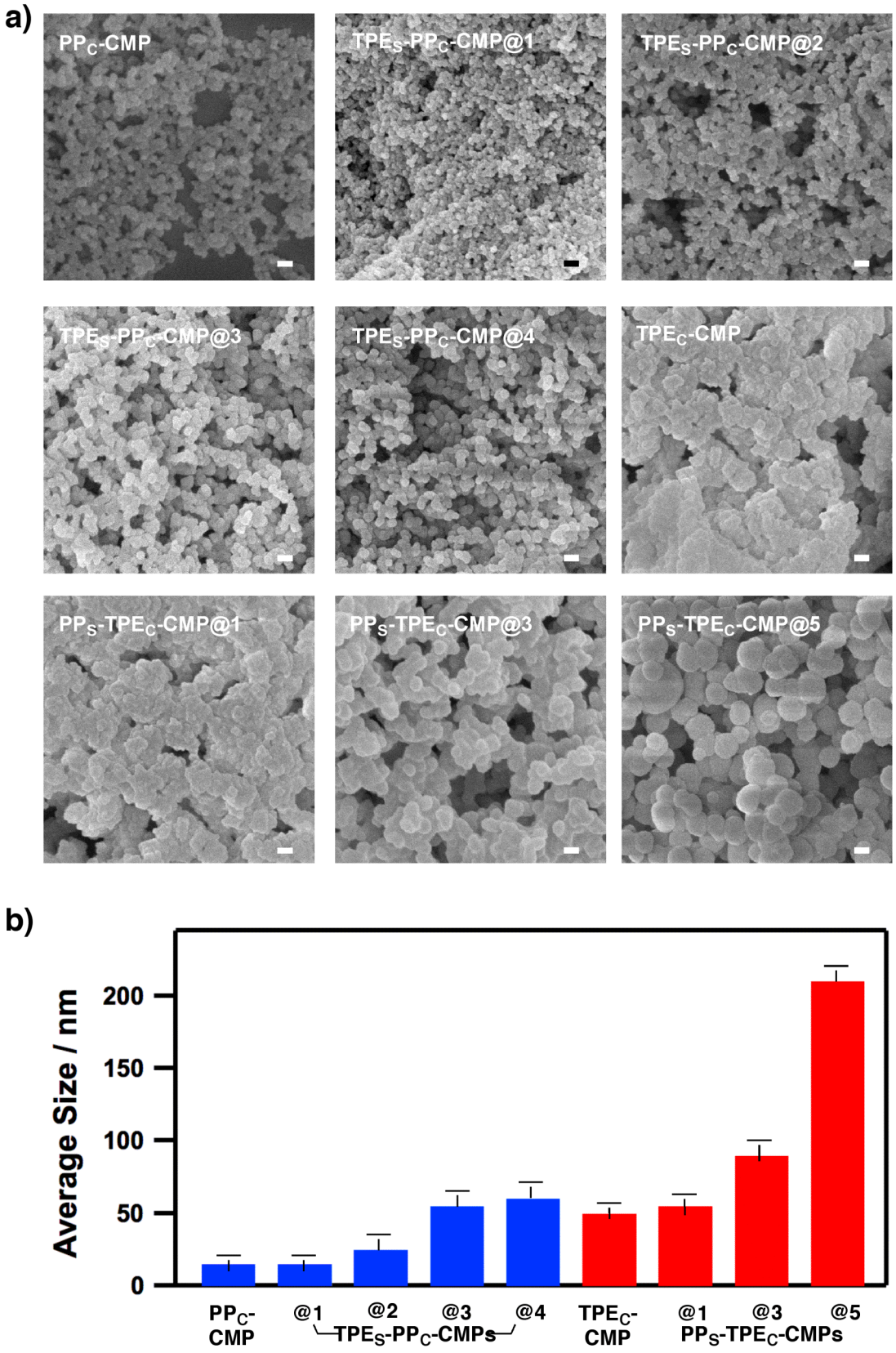


Figure S5. (a) FE SEM images of the CMPs (bar length is 100 nm). (b) Particle size of the CMPs, statistically evaluated from the FE-SEM images.

Section H. HR-TEM images

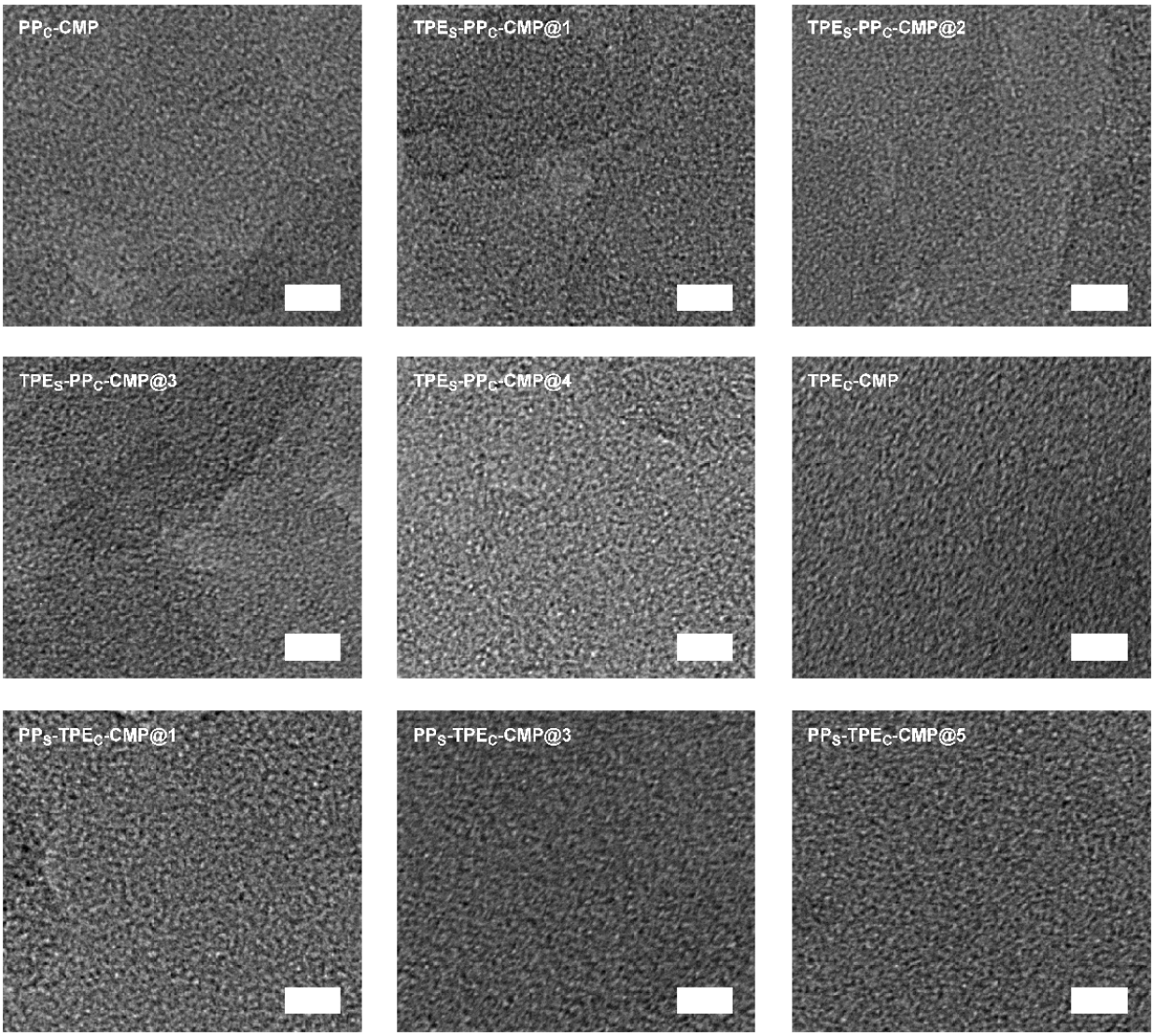


Figure S6. HR-TEM images of the CMPs (bar length is 10 nm).

Section I. Electronic absorption spectra

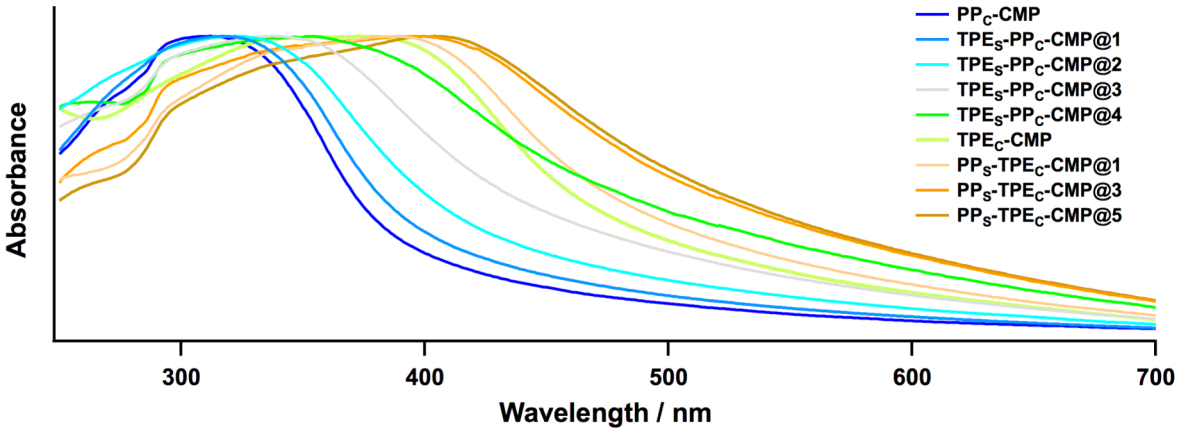


Figure S7. Electronic absorption spectra of the CMPs dispersed in THF at 25 °C.

Section J. Electronic absorption and fluorescence spectra of linear analogues

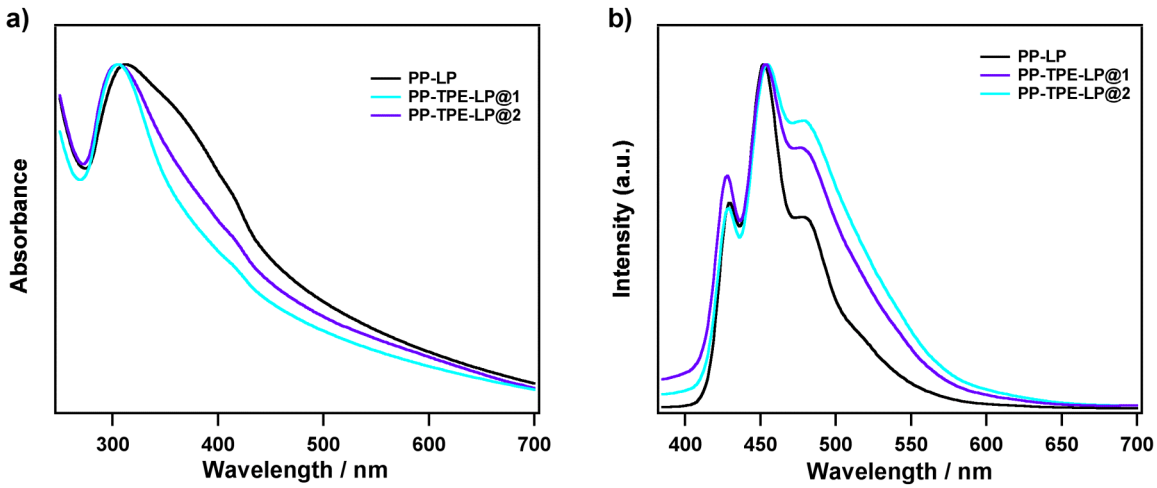


Figure S8. (a) Electronic absorption and (b) fluorescence spectra of PP-LP, PP-TPE-LP@1, and PP-TPE-LP@2 in THF at 25 °C.

Section K. CIE chromaticity diagram

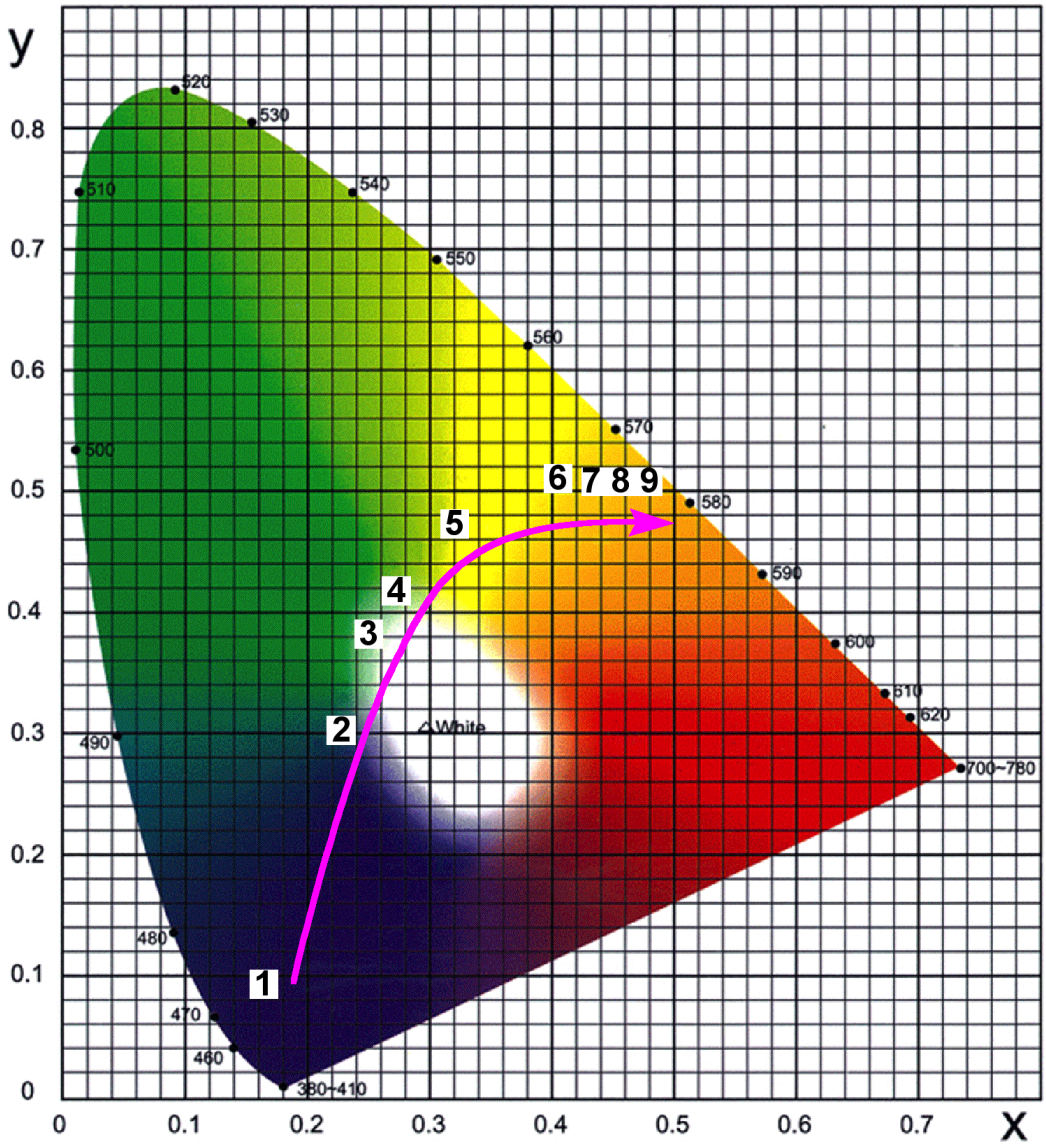


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Figure S9. CIE chromaticity diagram for CMPs (1: PP_C-CMP, 2: TPE_S-PP_C-CMP@1, 3: TPE_S-PP_C-CMP@2, 4: TPE_S-PP_C-CMP@3, 5: TPE_S-PP_C-CMP@4, 6: TPE_C-CMP, 7: PP_S-TPE_C-CMP@1, 8: PP_S-TPE_C-CMP@3, 9: PP_S-TPE_C-CMP@5).

Table S1. The CIE parameters of CMPs.

CIE	PP_C-CMP	TPE_S-PP_C-CMPs				TPE_C-CMP	PP_S-TPE_C-CMPs		
		@1	@2	@3	@4		@1	@3	@5
Solid	0.15, 0.10	0.21, 0.31	0.23, 0.39	0.25, 0.42	0.31, 0.48	0.43, 0.51	0.40, 0.52	0.44, 0.51	0.45, 0.51
THF Solution	0.15, 0.10	0.17, 0.20	0.21, 0.36	0.23, 0.41	0.30, 0.49	0.39, 0.53	0.40, 0.53	0.43, 0.51	0.45, 0.51

Section L. Fluorescence depolarization

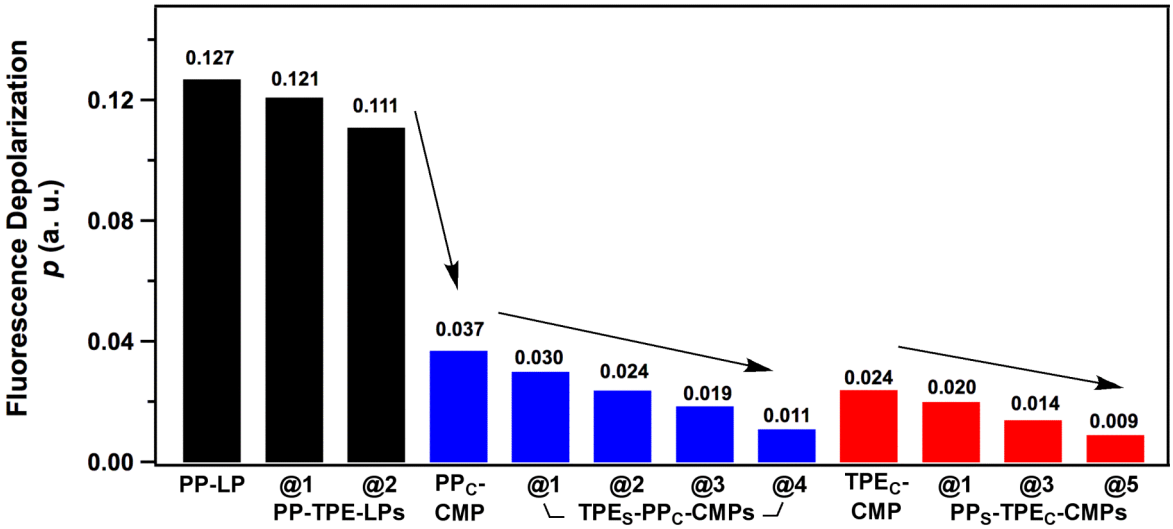

Figure S10. Fluorescence depolarization of the CMPs and linear analogues dispersed in PEG at 25 °C. No saturated tendency was observed for the core-shell CMPs.

Section M. Supporting references

S1. A. Schultz, S. Laschat, S. Diele, M. Nimtz, *Eur. J. Org. Chem*. 2003, 2829.

S2. (a) L. Liu, G. X. Zhang, J. F. Xiang, D. Q. Zhang, D. B. Zhu, *Org. Lett.* 2008**, 10***,* 4581. (b) R. Daik, W. J. Feast, A. S. Batsanov, J. A. K. Howard, *New J. Chem.* 1998, **22***,* 1047.