Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Preparation of 4-dicyanomethylene-2,6-distyryl-4*H*-pyran derivatives, their functional polystyrenes and study of their different aggregation induced emission behaviors

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Synthesis of 2,6-(dimethyl-4H-pyran-4-ylidene)malononitrile

2,6-Dimethyl-γ-pyrone (100 mmol, 12.41 g) and malononitrile (150 mmol, 9.91 g) were dissolved in 50 mL of acetic anhydride at 130 ^{o}C and stirred for 2 h under reflux. After cooling, the reaction mixture was poured into 1000 mL ice water. The precipitate was filtered and recrystallized twice from ethanol. Yield: 84% (84.3 mmol, 14.52 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.55 (s, 2H), 2.32 (s, 6H).

Synthesis of 4-[(2-hydroxy-ethyl)-methyl-amino]-benzaldehyde

2-(methylamino)ethanol (510 mmol, 38.31 g), 4-fluorobenzaldehyde (150 mmol, 18.62 g), potassium carbonate (430 mmol, 59.42 g), phase transfer catalyst 18-crown-6 (0.38 mmol, 100 mg) and 60 mL of dimethyl sulfoxide (DMSO) were refluxed in a two-necked round-bottomed flask under the protection of nitrogen at 100 ^{o}C for 5 days. The reaction mixture was cooled, poured into cold water, and extracted with chloroform. The organic layer was washed with water and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the residue was further purified by silica gel chromatography using petroleum/ethyl acetate mixture (2:1 by volume) as eluent. Yield: 71% (71.1 mmol, 19.10 g). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 9.65 (s, 1H), 7.68 (d, *J = 8.8 Hz*, 2H), 6.82 (d, *J = 8.8 Hz*, 2H), 4.80 (t, *J = 5.2 Hz*, 1H), 3.60 (m, 2H), 3.53 (dt, *J = 4.8 Hz*, *J = 5.6 Hz*, 2H), 3.05 (s, 3H).

Synthesis of 4-(2-hydroxyethoxy)benzaldehyde

To a solution of 4-hydroxybenzaldehyde (200 mmol, 24.40 g) and ethylene chlorohydrin (200 mmol, 16.00 g) in 60 mL of DMSO was added potassium carbonate (400 mmol, 55.20 g).The reaction mixture was stirred for 6 h at 100 ^{o}C and then poured into cold water and extracted with chloroform. The organic layer was washed with water and dried over anhydrous magnesium sulfate. Evaporation of the solvent afforded a residue, which was purified by silica gel chromatography using petroleum/ethyl acetate mixture (3:2 by volume) as eluent. Yield: 82% (164 mmol, 27.22 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.90 (s, 1H), 7.85 (d, *J = 9.3 Hz*, 2H), 7.03 (d, *J = 8.7 Hz*, 2H), 4.18 (t, *J = 9.0 Hz*, 2H), 4.02 (q, *J = 9.3 Hz*, 2H).

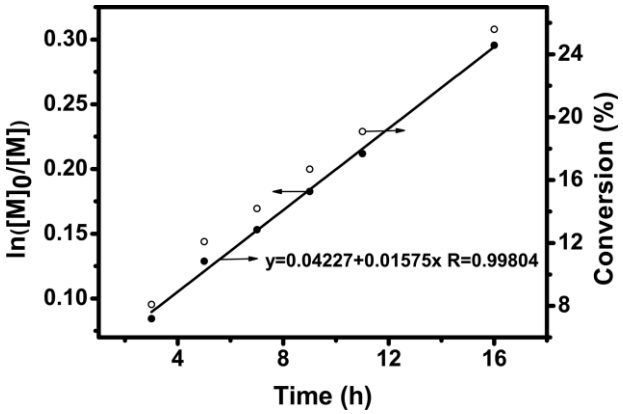


Fig. S1-1 The kinetic plot for the ATRP of St initiated by EtAmPy in cyclohexanone solution ($[initiator]_0$:$[CuBr]_0$:$[PMDETA]_0$:$[styrene]_0$ = 1:3:6:500, $[styrene]_0$ = 10.0 mol L^{-1}.).

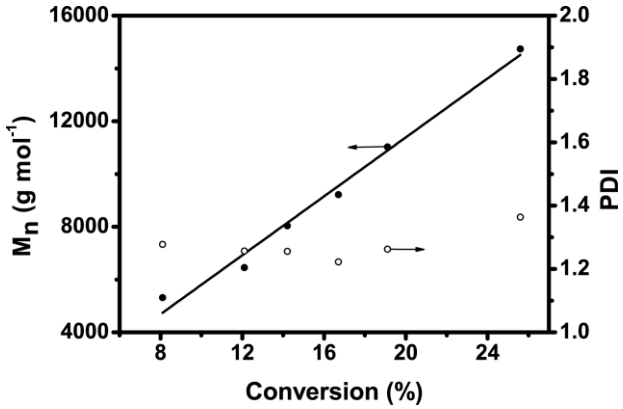


Fig. S1-2 Dependence of M_n and PDI with conversion for the polymerization of styrene initiated by EtAmPy in cyclohexanone solution ($[initiator]_0$:$[CuBr]_0$:$[PMDETA]_0$:$[styrene]_0$ = 1:3:6:500, $[styrene]_0$ = 10.0 mol L^{-1}).

TABLE S1 Initiators, Reaction time, Molecular weight and Monomer conversions of the Polymers made by ATRP

Initiator	Time(h)	Conversion (%)	$M_{n,GPC}$	PDI (M_w/M_n)
EtAmPy	3	8.1	5320	1.27
	5	12.1	6460	1.25
	7	14.2	8040	1.25
	9	16.7	9220	1.22
	11	19.1	11030	1.26
	16	25.6	14740	1.36
EtOxPy	5	11.8	6390	1.35

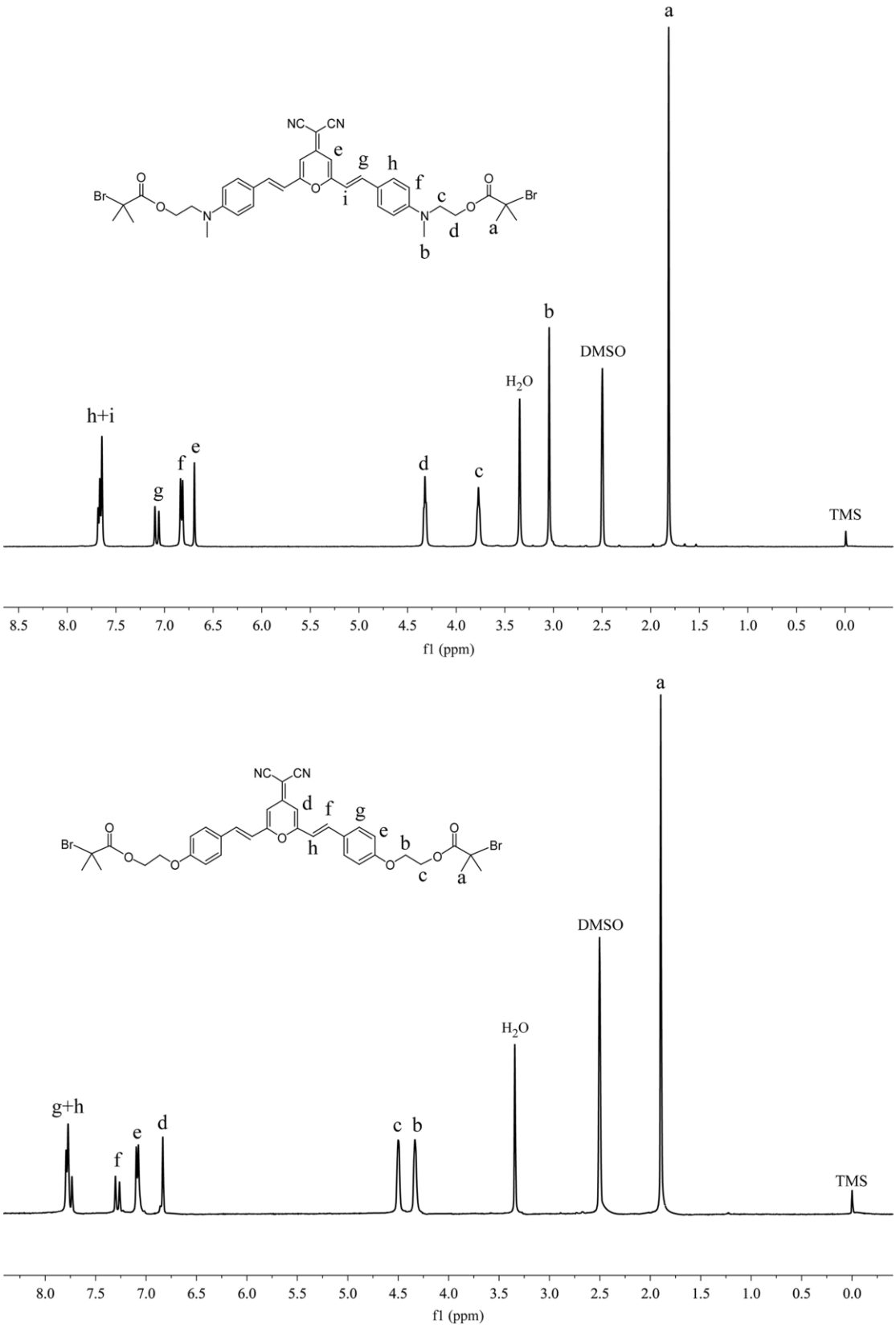


Fig. S2-1 ^{1}H NMR spectra of EtAmPy (top) and EtOxPy (bottom) at room temperature (400 MHz, DMSO-d_6).

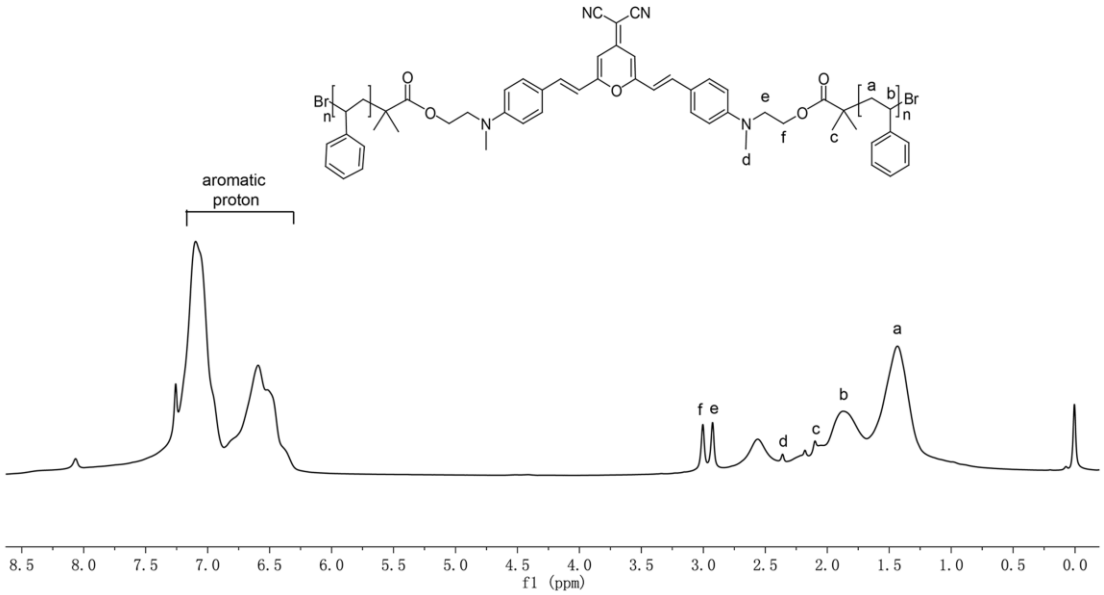
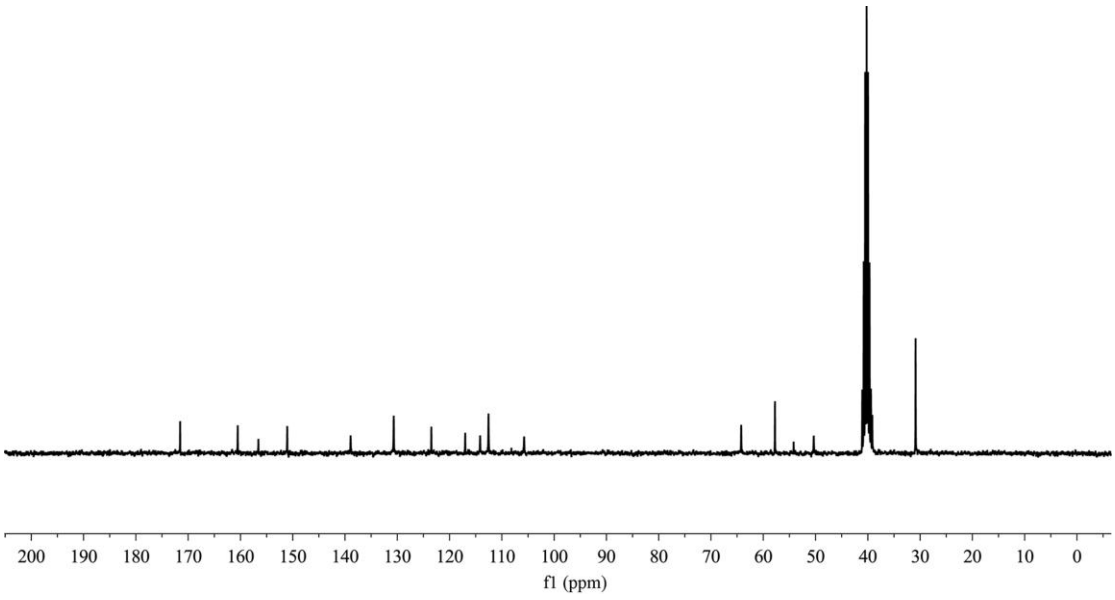


Fig. S2-2 ^{1}H NMR spectra of PSa at room temperature (400 MHz, $CDCl_3$).



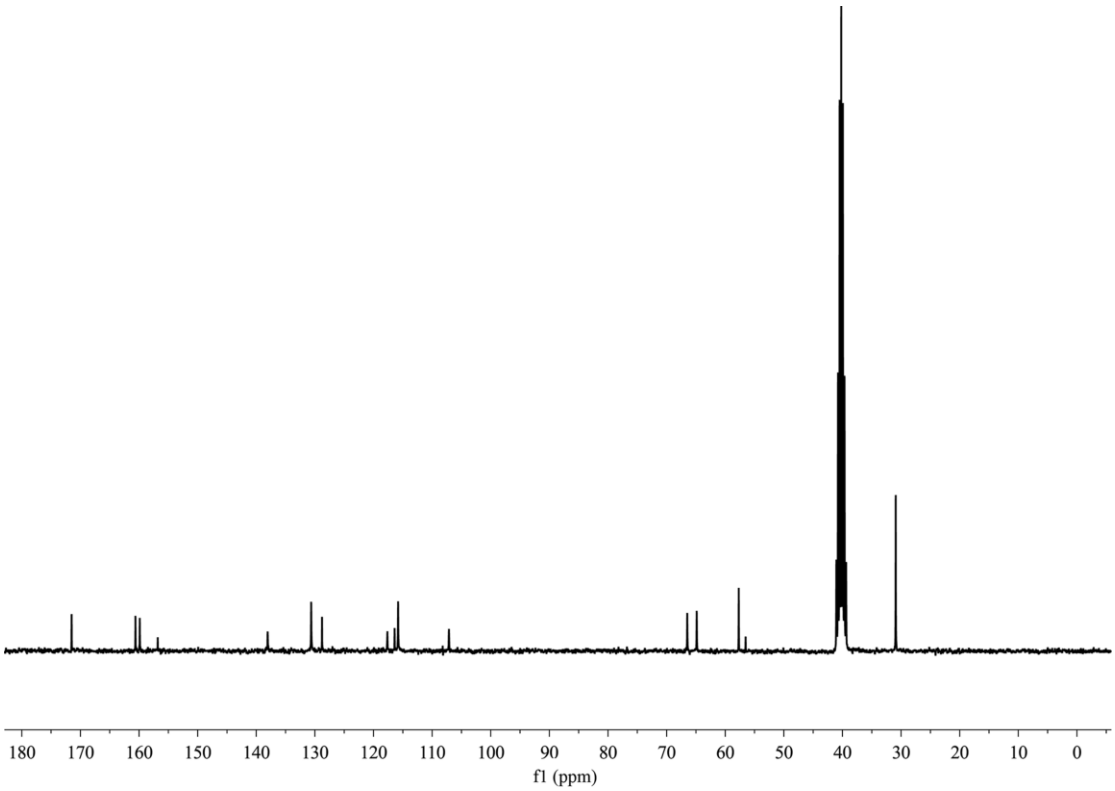
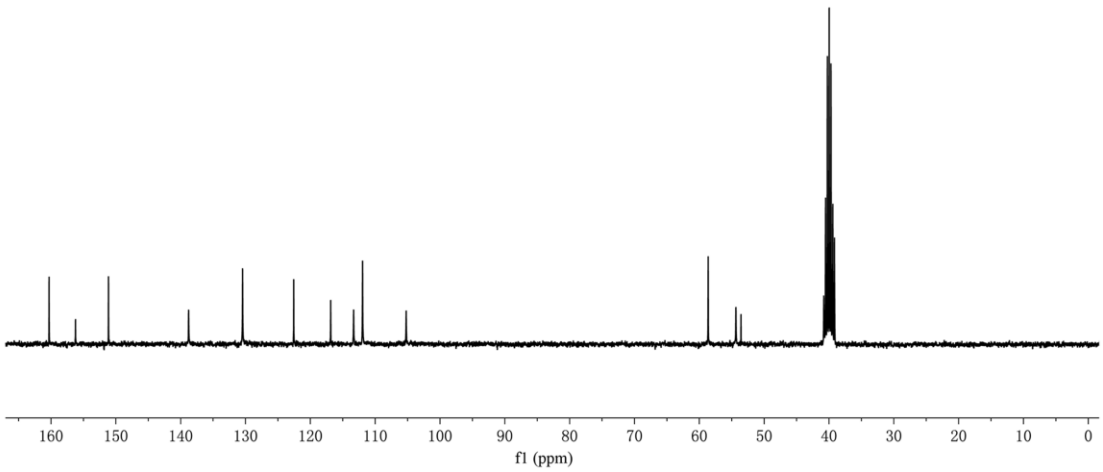


Fig. S3 ^{13}C NMR spectra of EtAmPy (top) and EtOxPy (bottom) at room temperature (300 MHz, DMSO-d_6).



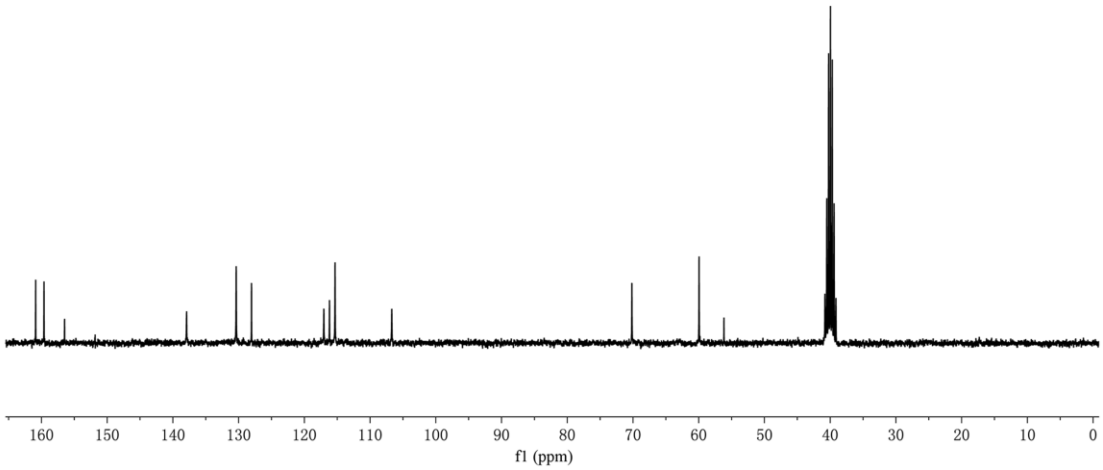


Fig. S4 ^{13}C NMR spectra of Compound 1 (top) and Compound 2 (bottom) at room temperature (300 MHz, DMSO-d_6).

Sample Name	YFJ-1	**Position**	Vial 1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	0	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
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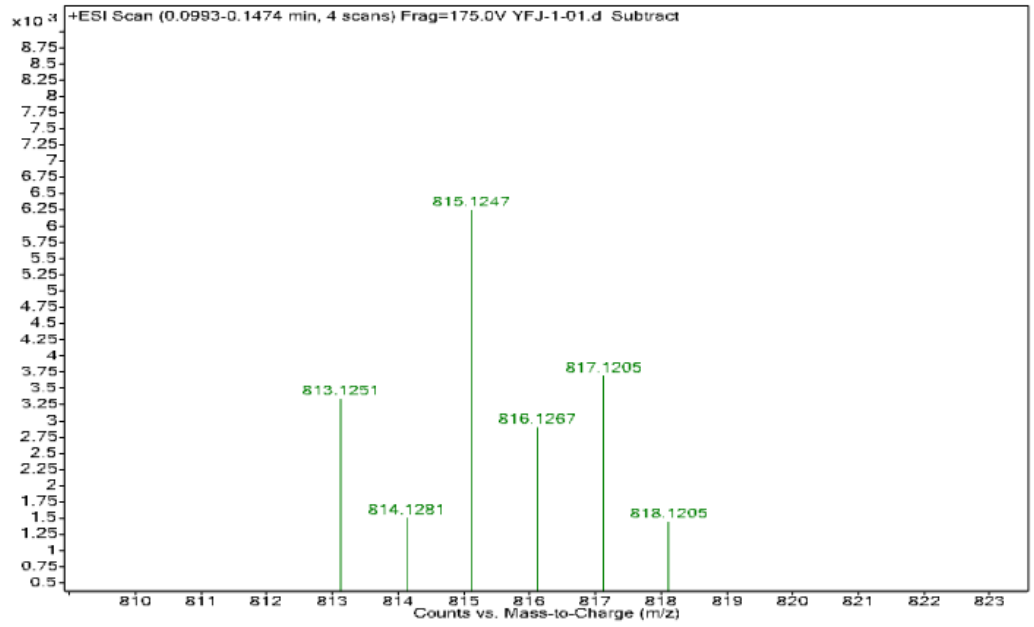
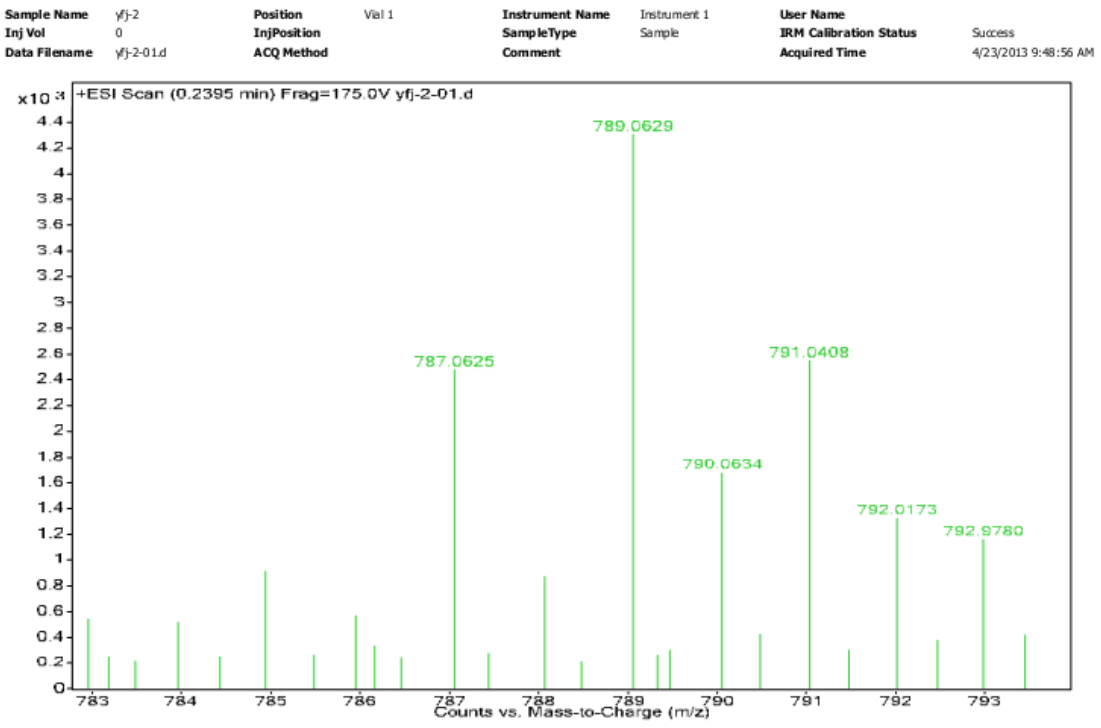


Formula Calculator

Formula (M)	Score	Mass	Calc m/z	Diff (ppm)	DBE	Ion Formula	m/z
C38 H40 Br2 N4 O5	99.49	790.1359	813.1258	0.84	20	C38 H40 Br2 N4 Na O5	813.1251

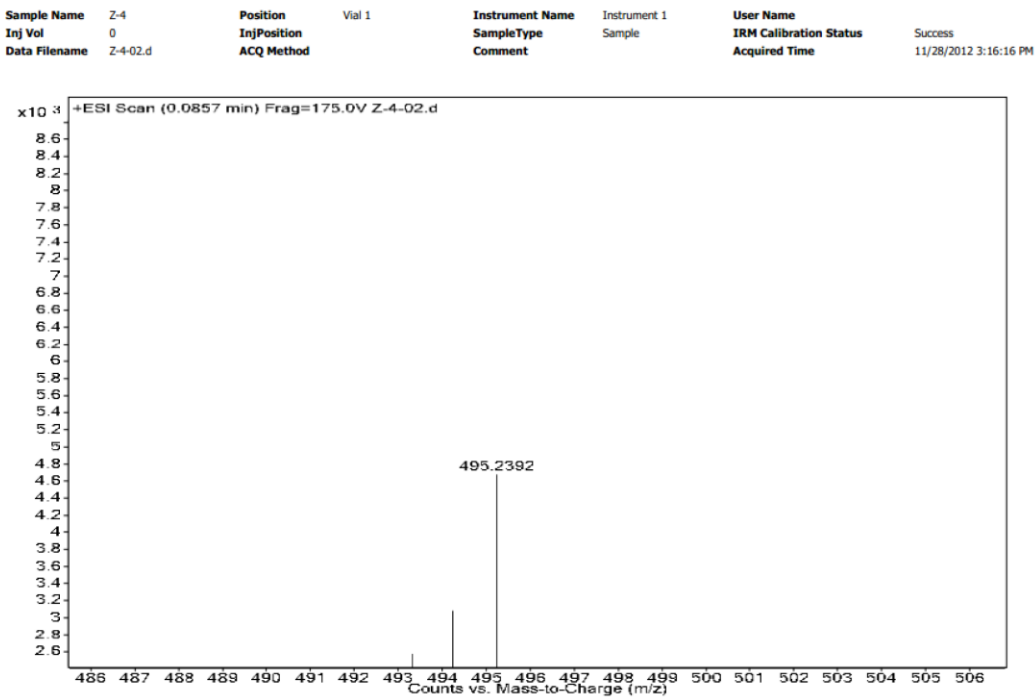
Fig. S5 LC-MS of EtAmPy



Formula Calculator

Formula (M)	Score	Mass	Calc m/z	Diff (ppm)	DBE	Ion Formula	m/z
C36 H34 Br2 N2 O7	100	764.0733	787.0625	0	20	C36 H34 Br2 N2 Na O7	787.0625

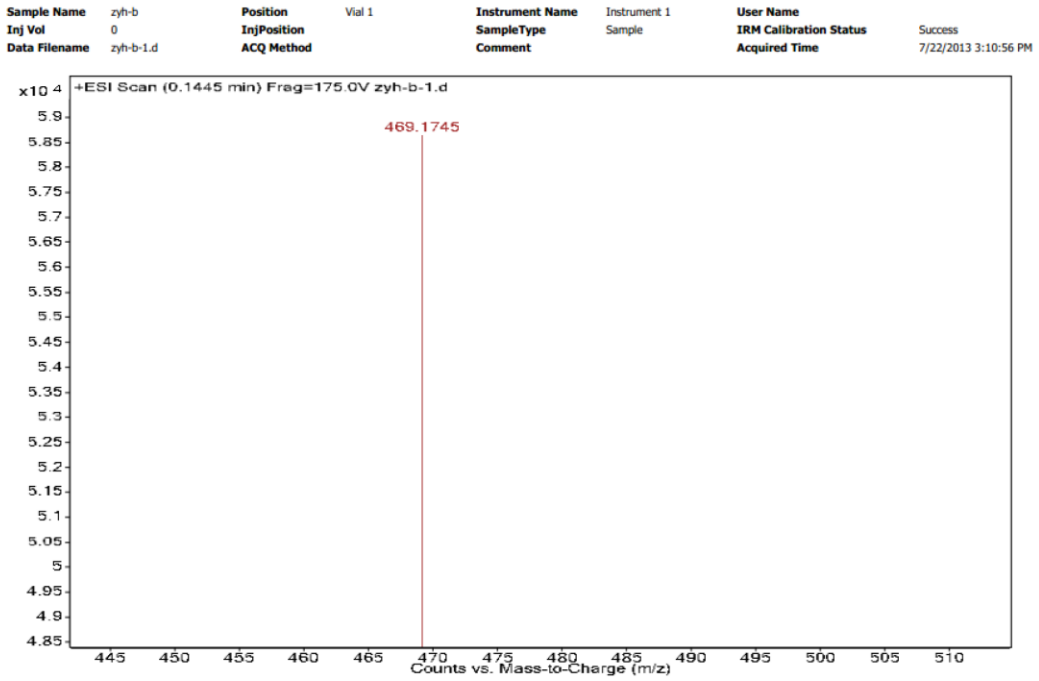
Fig. S6 LC-MS of EtOxPy



Formula Calculator

Formula (M)	Score	Mass	Calc m/z	Diff (ppm)	DBE	Ion Formula	m/z
C30 H30 N4 O3	99.96	494.2319	495.2391	-0.27	18	C30 H31 N4 O3	495.2392

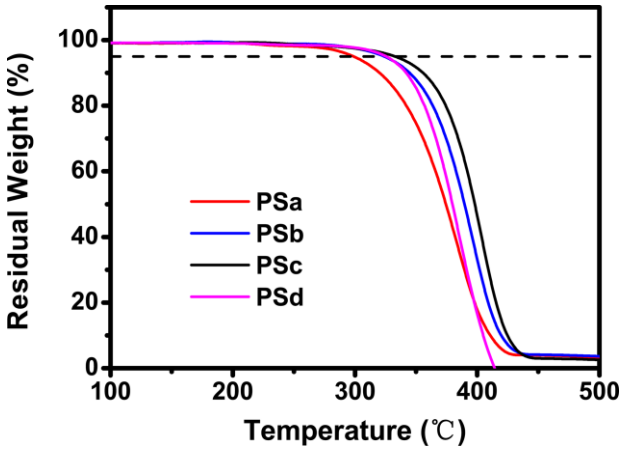
Fig. S7 LC-MS of Compound 1



Formula Calculator

Formula (M)	Score	Mass	Calc m/z	Diff (ppm)	DBE	Ion Formula	m/z
C28 H24 N2 O5	96.39	468.1672	469.1758	2.77	18	C28 H25 N2 O5	469.1745

Fig. S8 LC-MS of Compound 2



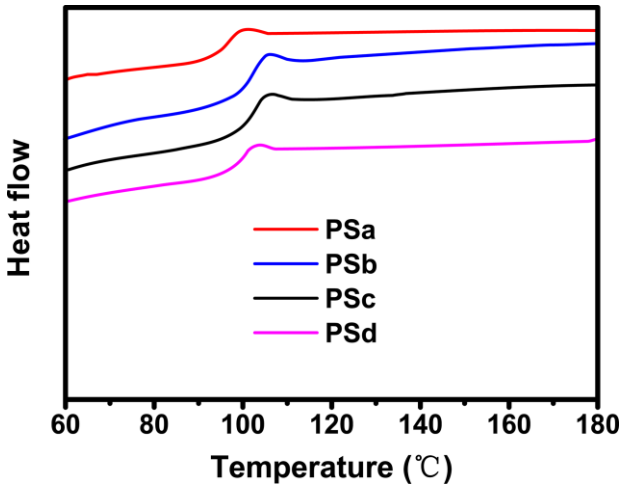


Fig. S9 TGA (top) and DSC (bottom) thermograms of polymers, recorded under N_2 at a heating rate of 10 and 20 ^{o}C /min, respectively.

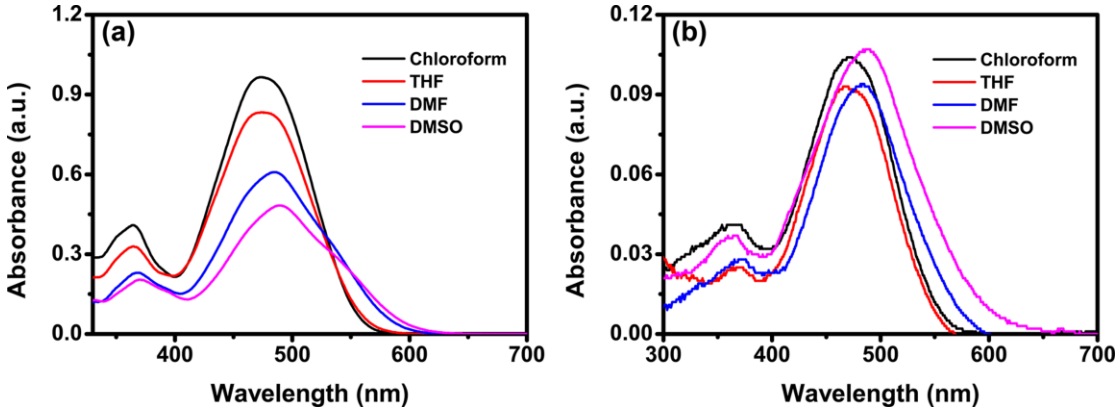


Fig. S10 Absorption spectra of (a) EtAmPy and (b) PSa in different polar solvents. Concentration: 10 μM.

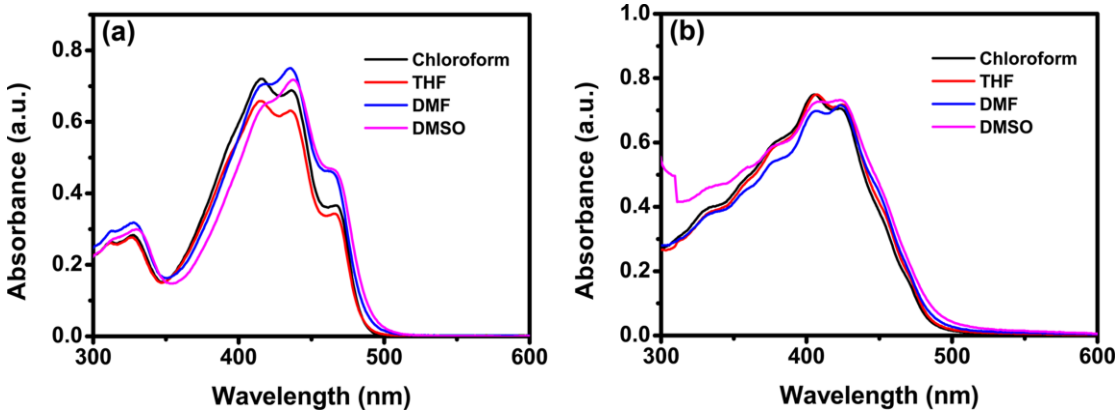


Fig. S11 Absorption spectra of (a) EtOxPy and (b) PSd in different polar solvents. Concentration: 10 μM.

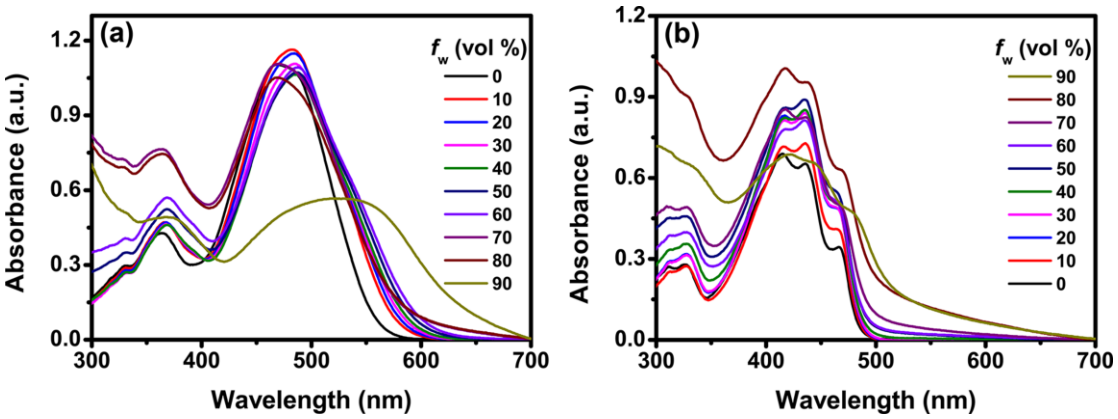


Fig. S12 Absorption spectra of (a) EtAmPy and (b) EtOxPy in the THF/water mixtures. Concentration: 10 μM.

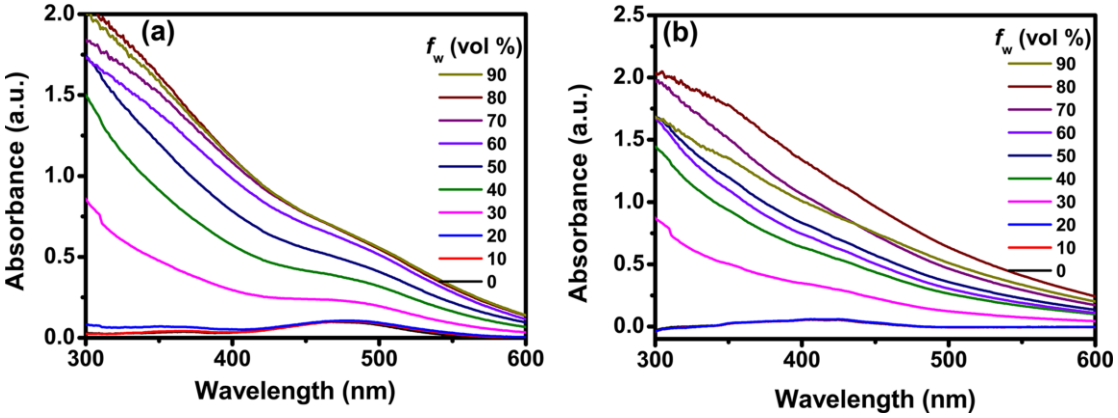


Fig. S13 Absorption spectra of (a) PSa and (b) PSd in the THF/water mixtures. Concentration: 10 μM

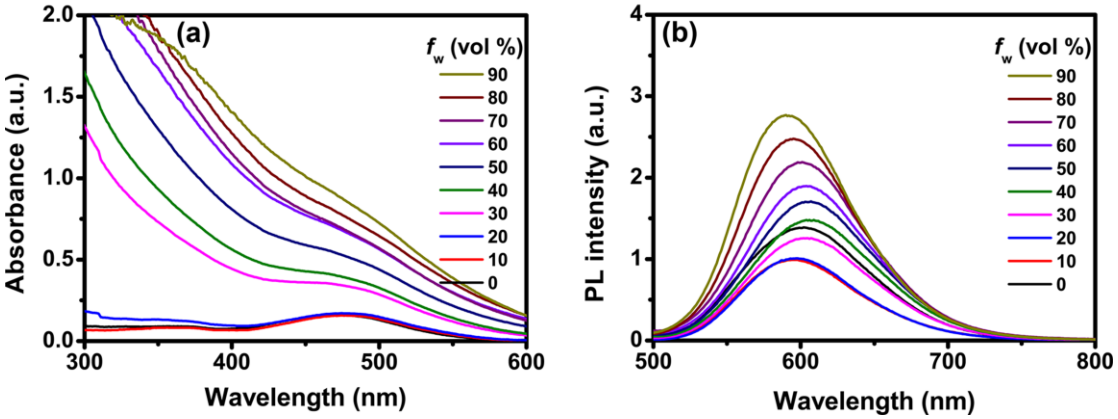


Fig. S14 (a) Absorption and (b) emission spectra of PSb in THF/water mixtures. Concentration: 10 μM. Excitation wavelength: 479 nm.

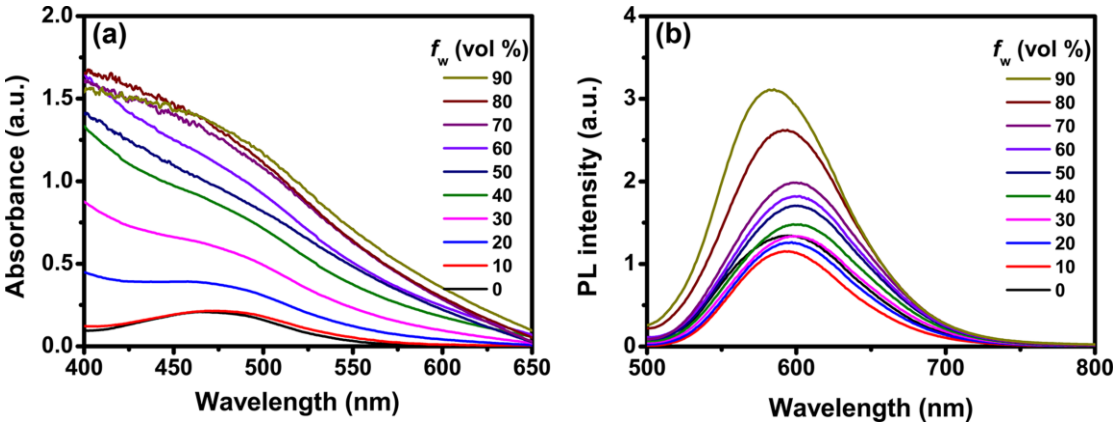


Fig. S15 (a) Absorption and (b) emission spectra of PSc in THF/water mixtures. Concentration: 10 μM. Excitation wavelength: 479 nm.

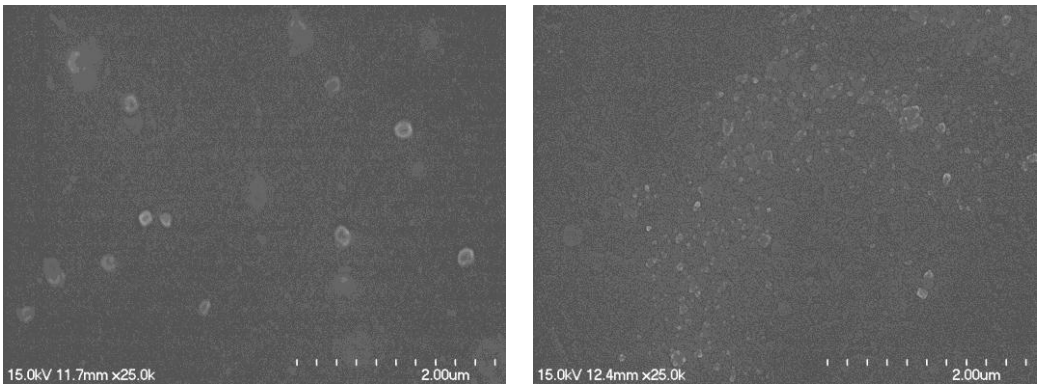


Fig. S16 SEM images of EtAmPy formed in THF/water (4:6 (left) and 1:9 (right) by volume). Scale bar is 2 μm.

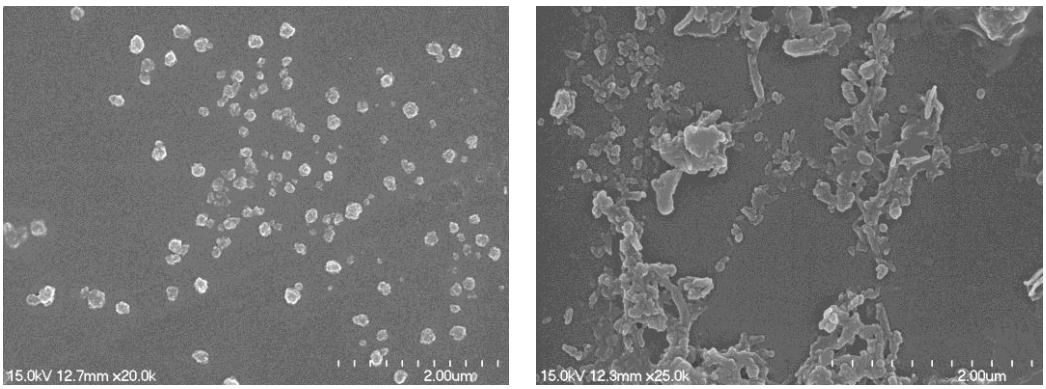


Fig. S17 SEM images of EtOxPy formed in THF/water (4:6 (left) and 1:9 (right) by volume). Scale bar is 2 μm.

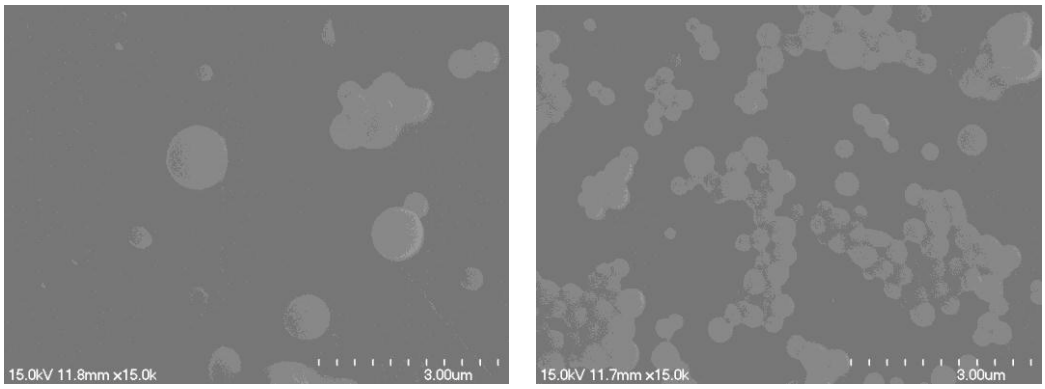


Fig. S18 SEM images of PSa formed in THF/water (4:6 (left) and 1:9 (right) by volume). Scale bar is 3 μm.

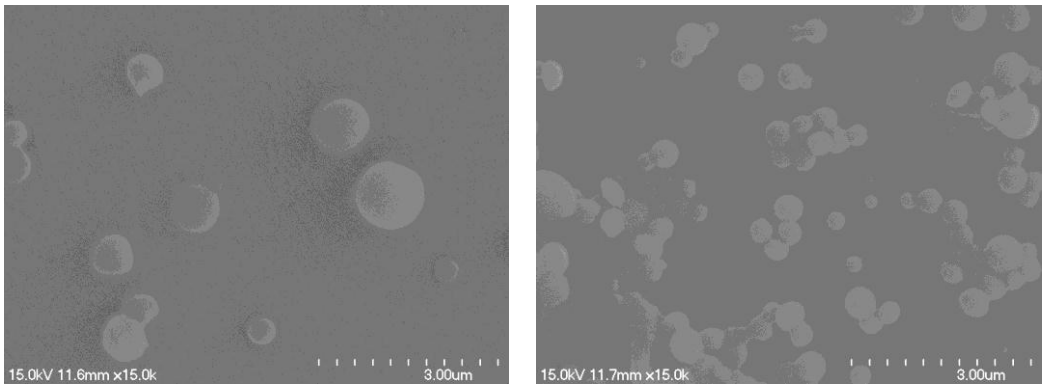


Fig. S19 SEM images of PSd formed in THF/water (4:6 (left) and 1:9 (right) by volume). Scale bar is 3 μm.

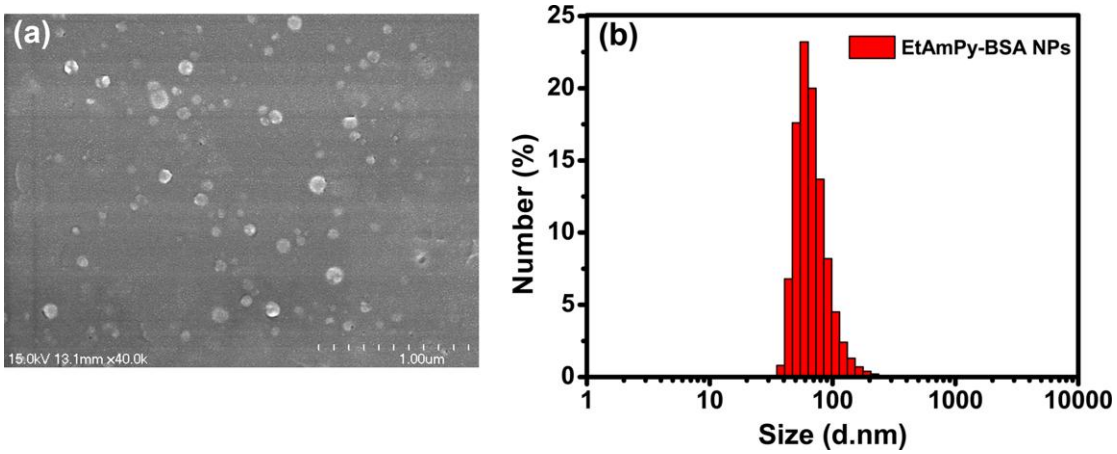


Fig. S20 (a) SEM image of EtAmPy-BSA NPs and (b) size distribution of the particles measured by DLS analysis. Scale bar is 1 μm.

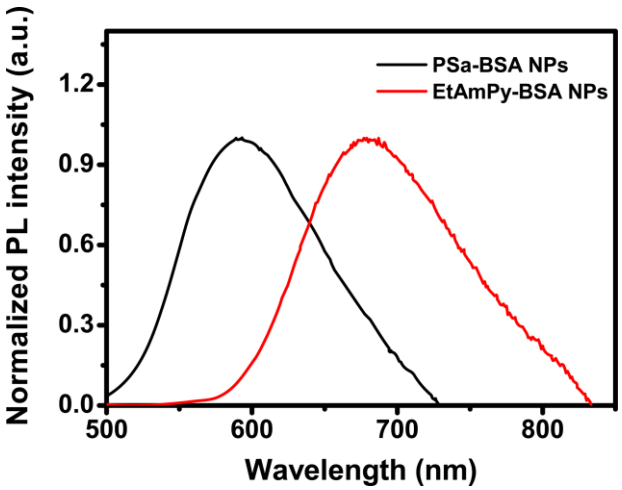


Fig. S21 Emission spectra of EtAmPy-BSA NPs and PSa-BSA NPs in physiological saline suspension. Excitation wavelength: 479 nm.

TABLE S2 Emission Characteristics of EtAmPy-BSA NPs and PSa-BSA NPs in physiological saline suspension[a]

Sample	λ_{em} [b] (nm)	Φ_F [c] (%)
EtAmPy-BSA NPs	680	1.18
PSa-BSA NPs	594	13.34

[a] Excitation wavelength: 479nm. [b] Emission maximum. [c] Fluorescent quantum yield estimated using fluorescein (Φ_F = 79% in 0.1 mol L^{-1} NaOH) as standard.

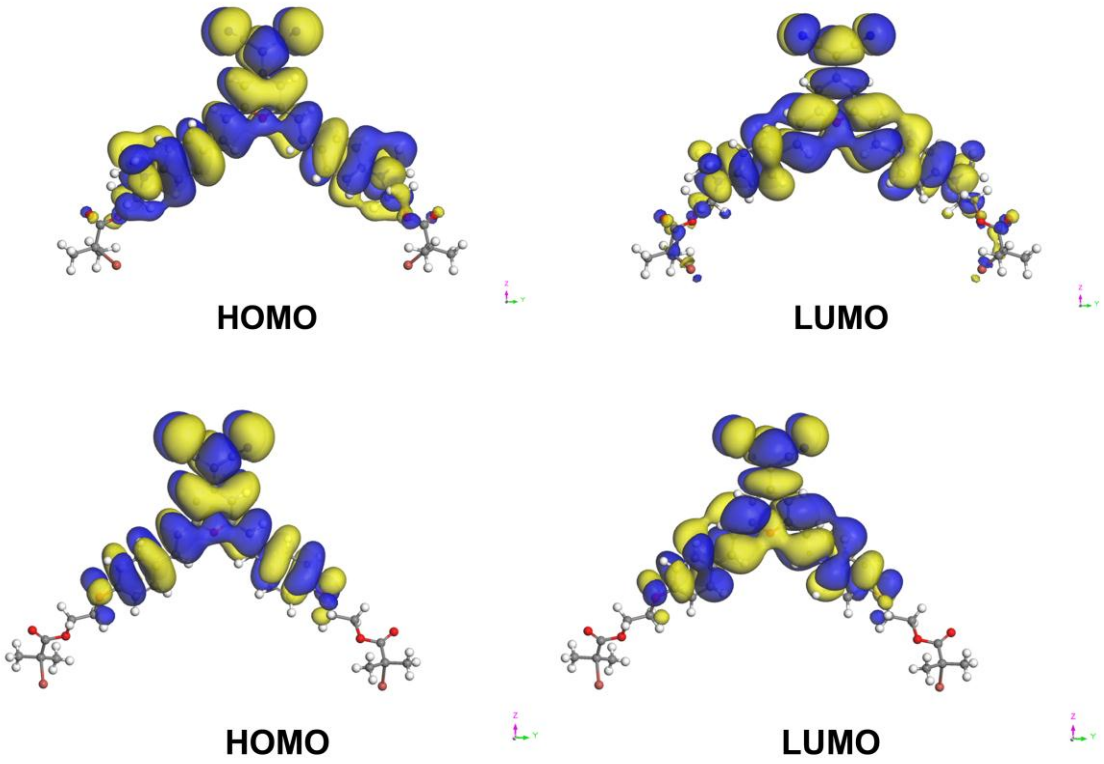


Fig. S22 Molecular orbital amplitude plots of HOMO and LUMO energy levels of EtAmPy (top) and EtOxPy (bottom).