

Electronic Supplementary Information (ESI)

Poly(arylene ynonylene) with aggregation-enhanced emission characteristic: fluorescent sensor for both hydrazine and picric acid detection

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Experimental

General information

THF was distilled from sodium benzophenone ketyl under dry nitrogen immediately prior to use. Compound **M1** and **M3** were prepared according to the literature methods.¹ All other chemicals and reagents were purchased from Aldrich and used as received without further purification. ¹H and ¹³C NMR spectra were measured on a Bruker AV 300 spectrometer in deuterated chloroform using tetramethylsilane (TMS; $\delta = 0$) as internal reference. IR spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer. UV-Vis spectra were measured on a Milton Roy Spectronic 3000 Array spectrophotometer. Photoluminescence was recorded on a Perkin-Elmer LS 55

spectrofluorometer. High resolution mass spectra were recorded on a GCT premier CAB048 mass spectrometer operating in a MALDT-TOF mode. Thermogravimetric analysis was carried on a TA TGA Q5000 under dry nitrogen at a heating rate of 10 °C/min. Number (M_n) and weight-average (M_w) molecular weights and polydispersity indices (PDI or M_w/M_n) of the polymers were estimated by a Waters Associates Gel Permeation Chromatography (GPC) system equipped with RI and UV detectors. THF was used as the eluent at a flow rate of 1.0 mL/min. A set of monodispersed linear polystyrenes covering the molecular weight range of 10^3 – 10^7 was used as standards for the molecular weight calibration.

Synthesis

Compound **M1** and **M3** were prepared according to the literature methods.¹ Their characterization data are given below.

1,2-Bis(4-ethynylphenyl)-1,2-diphenylethene (M1): ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 7.24 (m, 4H), 7.14 (m, 6H), 7.10 (m, 8H), 3.05 and 3.04 (2H, HC \equiv). ¹³C NMR (75 MHz, CDCl₃), δ (TMS, ppm): 144.86, 143.55, 141.73, 132.32, 132.18, 131.94, 131.87, 128.63, 128.47, 127.60, 127.52, 120.94, 84.41 (\equiv C–Ar), 78.12 (\equiv C–H). HRMS (MALDT-TOF): m/z 380.3151 (M^+ , calcd 380.1565).

1-(4-Ethynylphenyl)-1,2,2-triphenylethene (M3): ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 7.24 (d, 2H), 7.12 (m, 9H), 7.03 (m, 6H), 6.99 (d, 2H). ¹³C NMR (75 MHz, CDCl₃), δ (TMS, ppm): 145.36, 144.53, 144.26, 144.16, 144.04, 142.64, 140.94, 132.14, 132.00, 131.98, 131.91, 128.56, 128.51, 128.42, 128.39, 127.45, 127.36, 127.34, 127.14, 120.62, 84.27 (\equiv C–Ar), 77.96 (\equiv C–H). HRMS (MALDT-TOF): m/z 356.1577 (M^+ , calcd 356.1565).

1-[4-(2-Benzoyl ethynyl)phenyl]-1,2,2-triphenylethene (MC4): Into a 50 mL round bottom flask were placed 1.0 g (2.8 mmol) of **M3**, 21 mg (0.03 mmol) of Pd(PPh₃)₂Cl₂, 17 mg (0.09 mmol) of CuI and 30 mL of distilled THF in an atmosphere of nitrogen. 0.4 mL (2.8 mmol) of triethylamine was then injected into the flask and the mixture was stirred at room temperature for 10 min. 0.36 mL (3.1 mmol) of benzoyl chloride was added into the mixture and the mixture was stirred at room temperature for another 3 h. The organic layer was extracted with 50 mL

dichloromethane three times. The combined organic layers were washed with saturated brine solution and dried over anhydrous MgSO_4 . The solvent was evaporated and the resulting crude product was purified on a silica-gel column using ethyl acetate/hexane mixture (1/20 v/v) as eluent to afford **MC4** as a light yellow solid in 95% yield. ^1H NMR (300 MHz, CDCl_3), δ (TMS, ppm): 8.20 (d, 2H), 7.62 (t, 1H), 7.50 (t, 2H), 7.43 (d, 2H), 7.16–7.01 (m, 17H). ^{13}C NMR (75 MHz, CDCl_3), δ (TMS, ppm): 178.60 (C=O), 147.56, 143.84, 143.77, 143.64, 143.27, 140.45, 137.60, 134.73, 133.22, 132.33, 132.00, 131.90, 130.24, 129.26, 128.60, 128.40, 127.64, 127.46, 94.31 ($\equiv\text{C}-\text{Ar}$), 87.91 ($\equiv\text{C}-\text{C}=\text{O}$). HRMS (MALDI-TOF): m/z 460.1602 (M^+ , calcd 460.1856).

1-[4-(3-Phenyl-5-pyrazolyl)phenyl]-1,2,2-triphenylethene (MC6): Into a 50 mL round bottom flask was added 10 mL THF solution of 0.5 g (1 mmol) of **MC4**. 0.1 mL of hydrazine monohydrate was then injected and the mixture was stirred for 30 min. The mixture was extracted with 30 mL dichloromethane three times. The combined organic layers were washed with saturated brine solution and dried over anhydrous MgSO_4 . The solvent was evaporated and the crude product was purified on a silica-gel column using ethyl acetate/hexane mixture (1/5 v/v) to afford the target product **MC6** as a white solid in 90% yield. ^1H NMR (300 MHz, CDCl_3), δ (TMS, ppm): 7.71 (m, 2H), 7.46 (m, 2H), 7.37 (m, 2H), 7.12–7.03 (m, 18H), 6.78 (s, 1H). ^{13}C NMR (75 MHz, CDCl_3), δ (TMS, ppm): 144.63, 144.30, 142.13, 141.05, 132.58, 132.07, 132.01, 129.57, 128.94, 128.51, 128.42, 128.31, 127.29, 127.24, 127.19, 126.27, 125.48, 100.74. HRMS (MALDI-TOF): m/z 474.1998 (M^+ , calcd 474.2100).

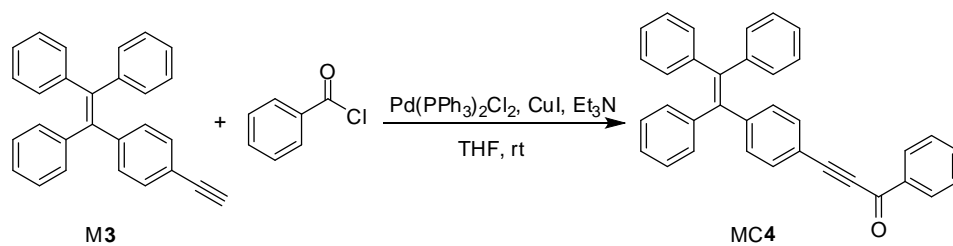
P1/2: All the polymerization reactions were carried out under nitrogen using standard Schlenk technique. A typical experimental procedure for the polymerization of **M1** and **M2** is given below. Into a 15 mL Schlenk tube with a three way stopcock on the side arm was placed 76.1 mg (0.2 mmol) of **M1**, 2.8 mg (0.004 mmol) of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, 2.3 mg (0.012 mmol) of CuI and 3 mL distilled THF in an atmosphere of nitrogen. 0.06 mL (0.4 mmol) of triethylamine was then injected into the flask and the mixture was stirred at room temperature for 10 min. 1 mL of distilled THF solution of 40.5 mg (0.2 mmol) of terephthaloyl dichloride (**M2**) was added and the

mixture was stirred at room temperature for 3 h. The mixture was diluted by adding 10 mL THF and the solution was then added dropwise to 200 mL methanol through a cotton filter under stirring. The precipitate was allowed to stand overnight and collected by filtration. The brown polymer was washed with methanol and dried under vacuum at room temperature to a constant weight. Characterization data for **PI/2**: brown powder; yield: 85.9%. M_w 8900; M_w/M_n 2.0 (Table S1, entry 9). IR (KBr thin film), ν (cm^{-1}): 2191 ($\text{C}\equiv\text{C}$ stretching), 1645 ($\text{C}=\text{O}$ stretching). ^1H NMR (300 MHz, CDCl_3), δ (TMS, ppm): 8.29, 7.50–7.40, 7.20–6.95. ^{13}C NMR (75 MHz, CDCl_3), δ (TMS, ppm): 177.61, 147.23, 142.97, 142.19, 141.20, 133.44, 132.38, 132.00, 130.30, 128.92, 128.11, 118.58, 95.39 ($\text{C}\equiv\text{C}-\text{Ar}$), 88.05 ($\text{C}\equiv\text{C}-\text{C}=\text{O}$).

Table S1 Polymerization of **M1** and **M2**^a

entry ^b	[Pd] (mM)	time (h)	[Et ₃ N] (equiv)	yield (%)	M_w^c	M_w/M_n^c
1	0.5	3	1	13.5	3600	1.5
2	5	3	1	76.1	8400	2.0
3	10	3	1	84.7	12200	2.3
4	1	3	1	45.2	3900	1.6
5	1	8	1	44.1	5100	1.9
6	1	20	1	55.0	4600	1.7
7	5	3	1	70.0	39100	3.8
8	5	3	1	67.7	6000	1.9
9	1	3	1	85.9	8900	2.0
10	1	3	1.25	45.3	5100	2.1
11	1	3	1.50	29.9	5100	1.8

^a Carried out under nitrogen at room temperature in the presence of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI and Et_3N in THF. $[\text{M1}] = [\text{M2}] = 0.05$ M. ^b Addition sequence: one-pot (entry 1–6), **M2** to mixture of **M1** and catalysts (entry 7 and 9–11), **M1** to mixture of **M2** and catalysts (entry 8). ^c Determined by GPC in THF on the basis of a linear polystyrene calibration.



Scheme S1 Preparation of model compound MC4.

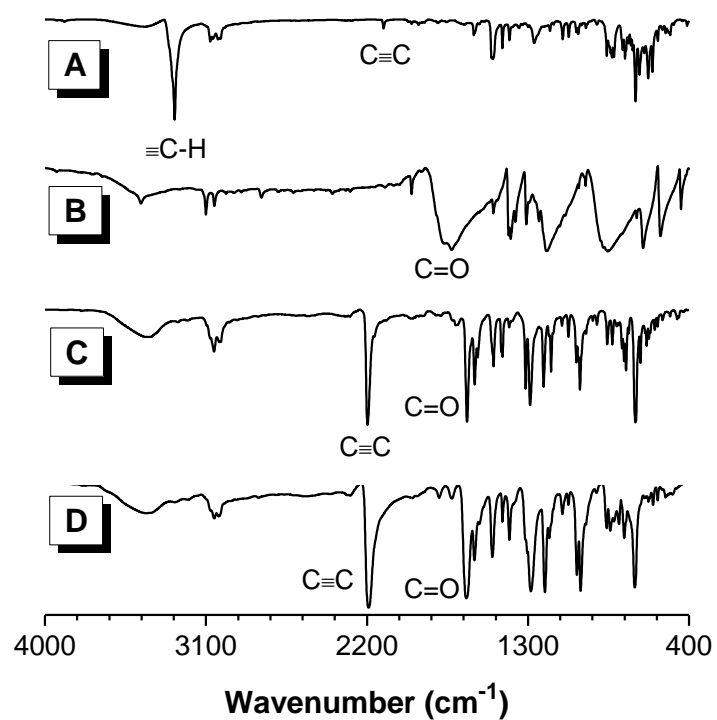


Fig. S1 IR spectra of (A) M1, (B) M2, (C) MC4 and (D) P1/2.

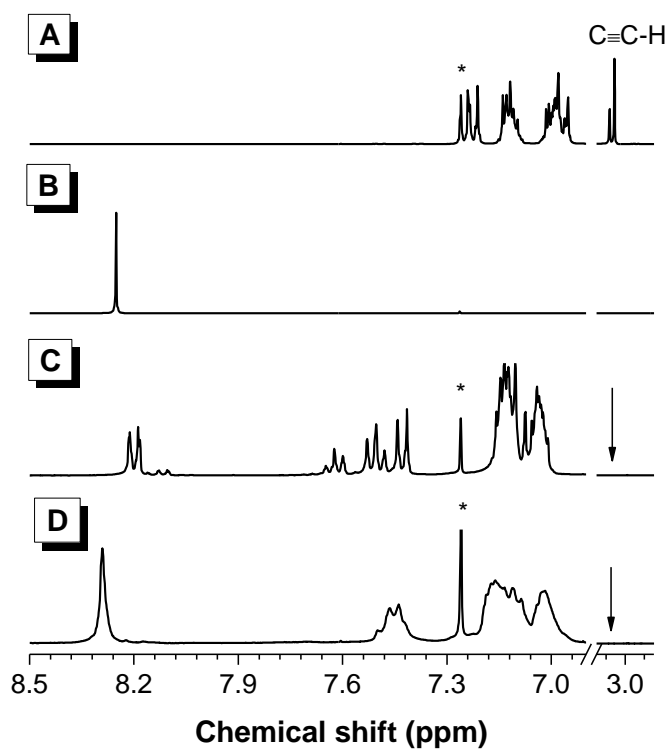


Fig. S2 ^1H NMR spectra of (A) M1, (B) M2, (C) MC4 and (D) P1/2 in chloroform-*d*.
The solvent peaks were marked with asterisks.

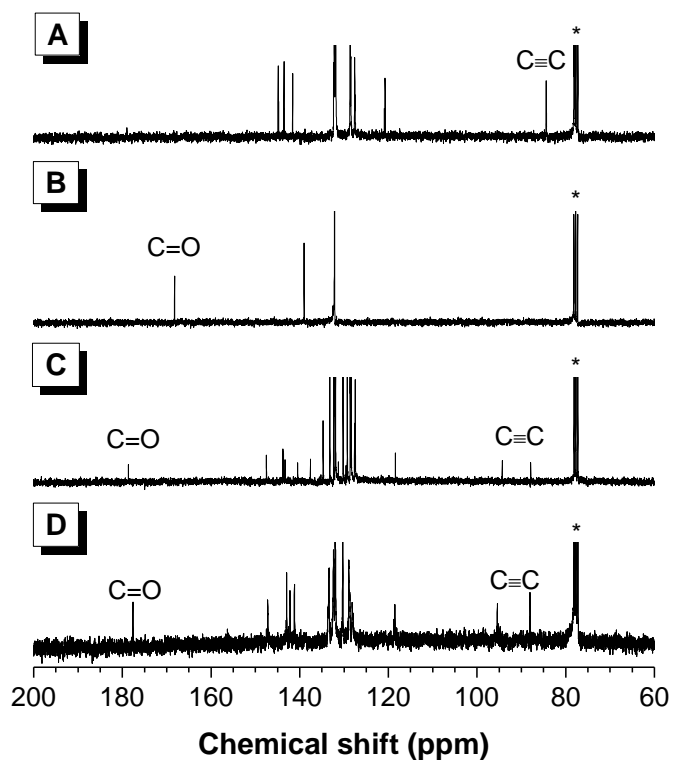


Fig. S3 ^{13}C NMR spectra of (A) M1, (B) M2, (C) MC4 and (D) P1/2 in chloroform-*d*.
The solvent peaks were marked with asterisks.

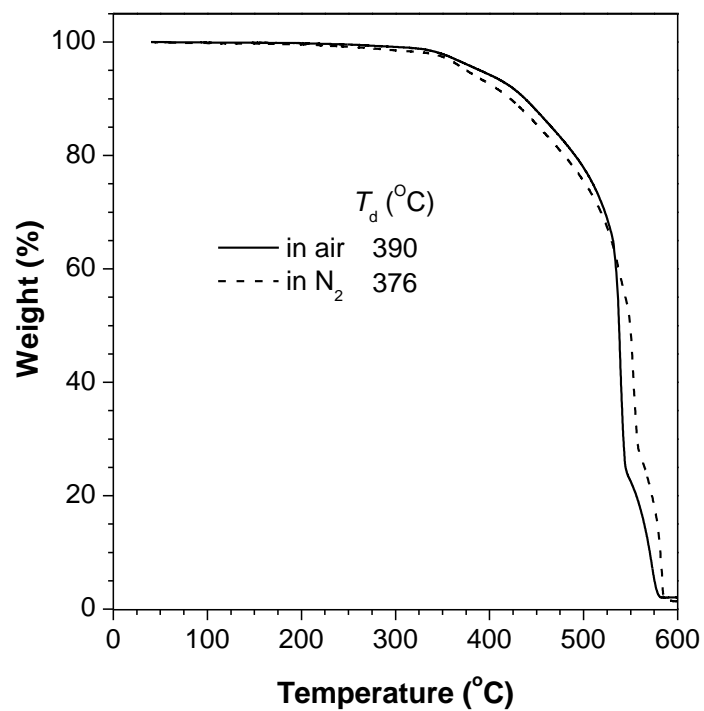


Fig. S4 TGA thermograms of P1/2 recorded under nitrogen and in air at a heating rate of 10 °C/min.

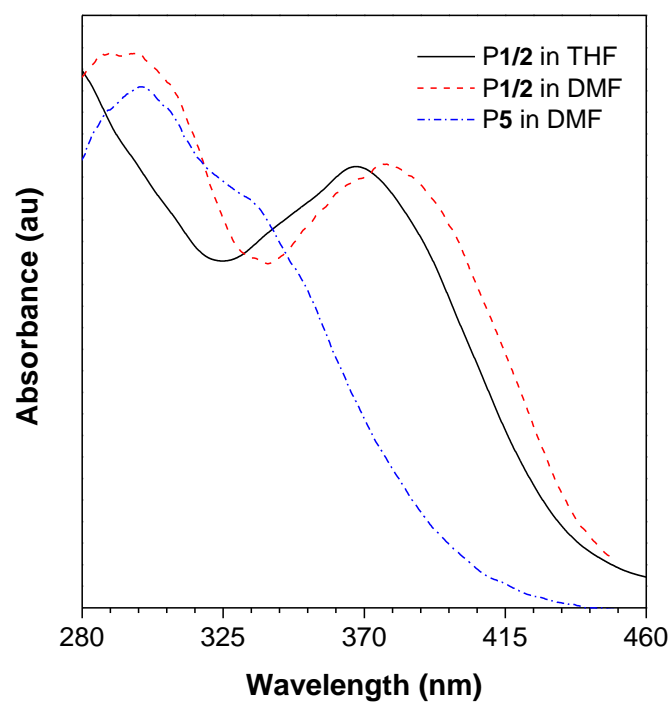


Fig. S5 Normalized UV spectra of P1/2 in THF and DMF, and P5 in DMF at room temperature. Concentration: 10^{-5} M.

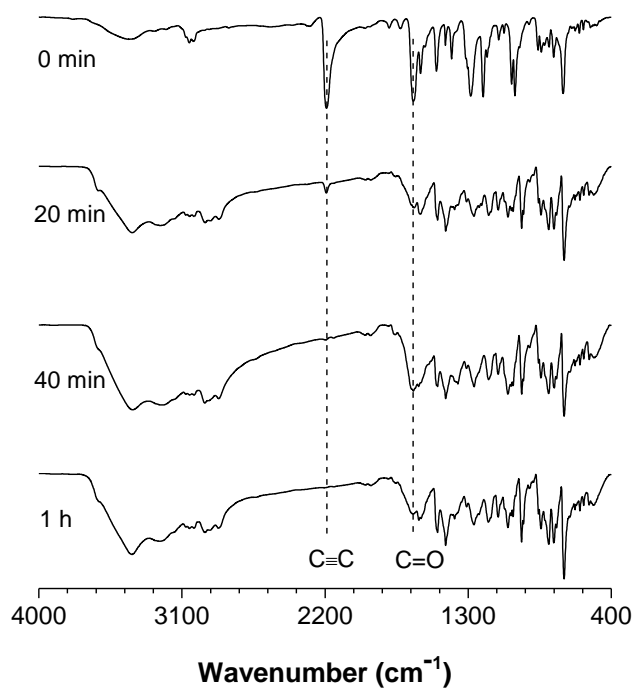
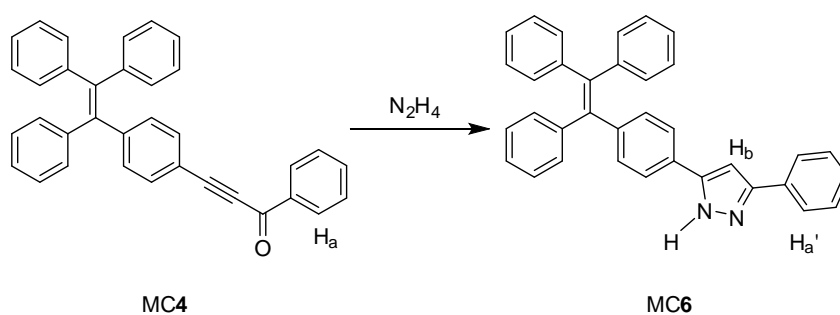


Fig. S6 IR spectra of P1/2 before and after reaction with hydrazine in THF solution at different reaction times.



Scheme S2 Investigation on the hydrazine detection mechanism via model reaction.

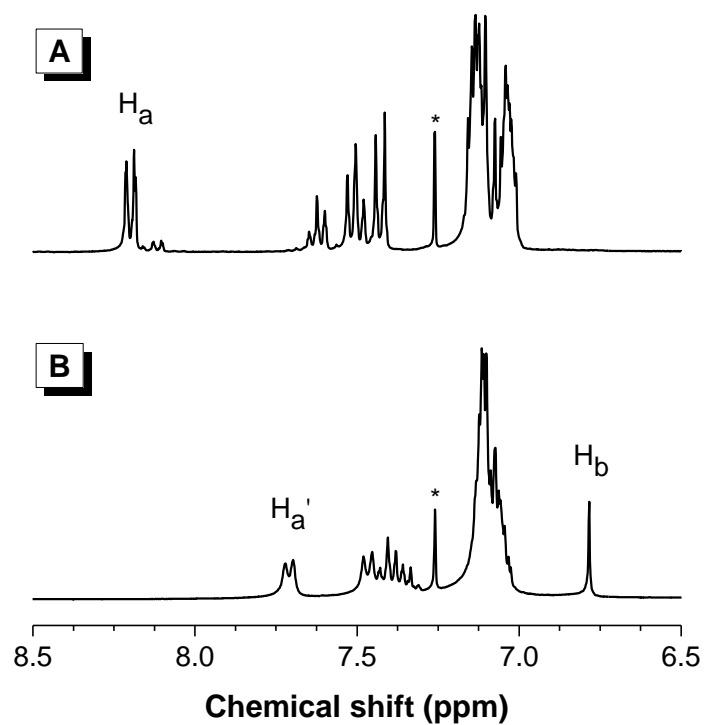


Fig. S7 ¹H NMR spectra of (A) MC4 and (B) MC6 in chloroform-*d*. The solvent peaks were marked with asterisks.

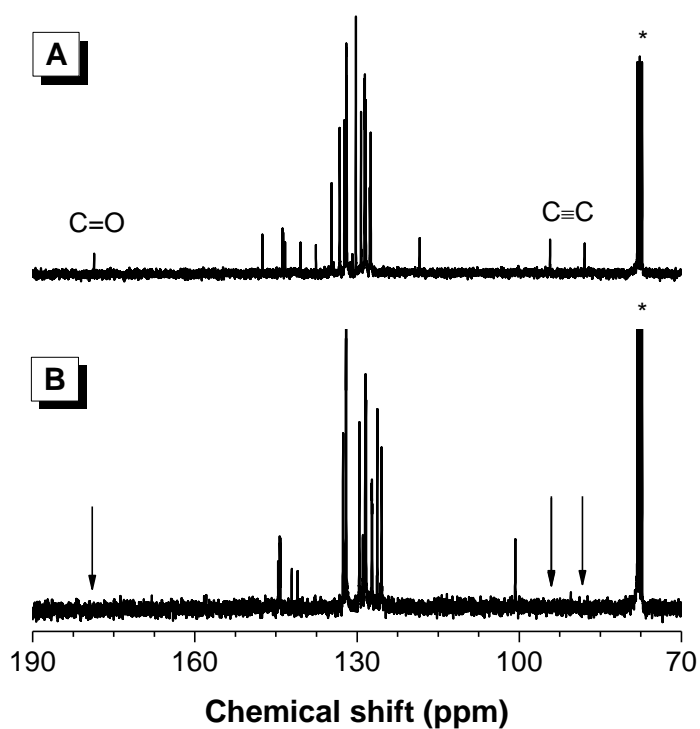


Fig. S8 ¹³C NMR spectra of (A) MC4 and (B) MC6 in chloroform-*d*. The solvent peaks were marked with asterisks.

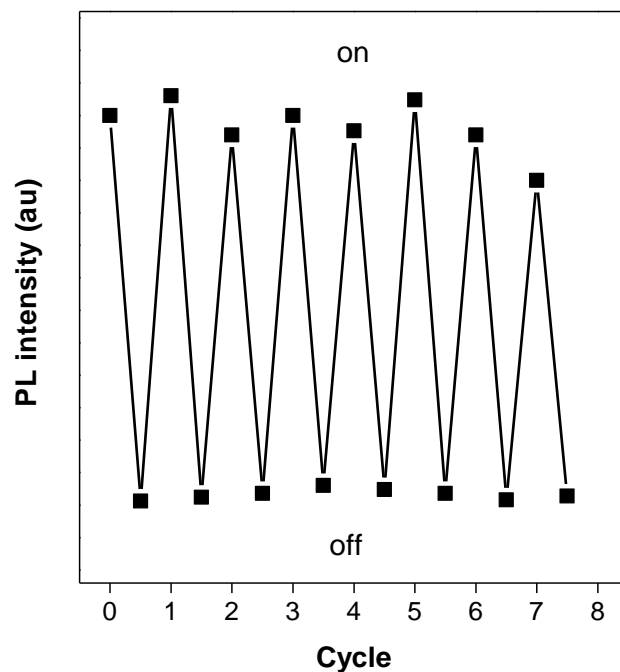


Fig. S9 Reversibly switching the light emission of P1/2 coated on glass slide between fluorescence ‘off’ and ‘on’ states by repeatedly dipping into aqueous PA solution (2 mg/mL) and washing with distilled water. Excitation wavelength: 360 nm.

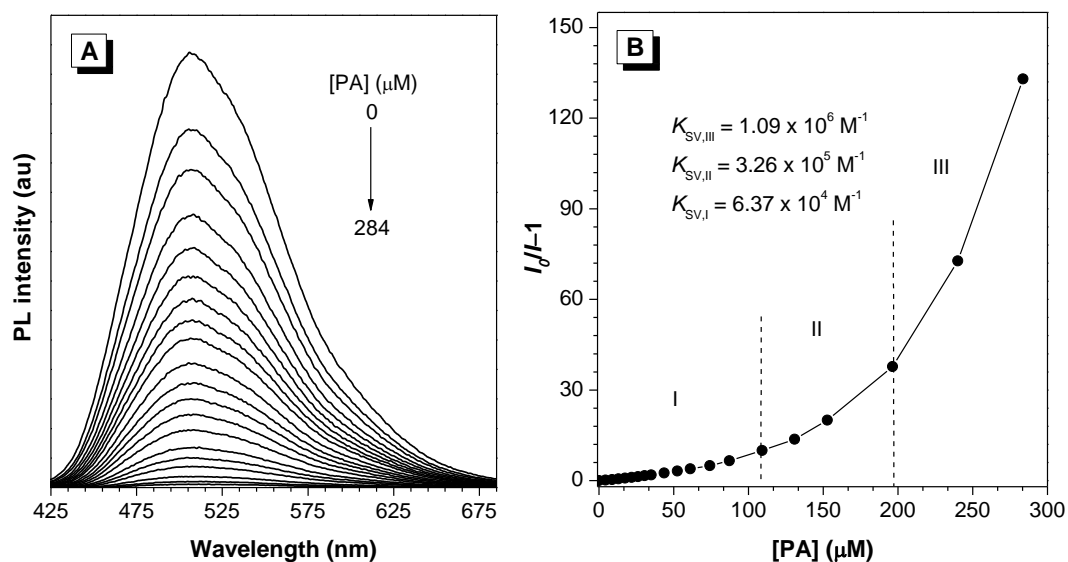


Fig. S10 (A) PL spectra of P5 in DMF/water mixtures (2:3 v/v) with different concentrations of picric acid (PA) at room temperature. (B) Plots of $(I_0/I - 1)$ values versus PA concentrations in DMF/water mixtures (2:3 v/v) of P5. I_0 = peak intensity at $[PA] = 0$. Concentration: 10^{-5} M; excitation wavelength: 360 nm.

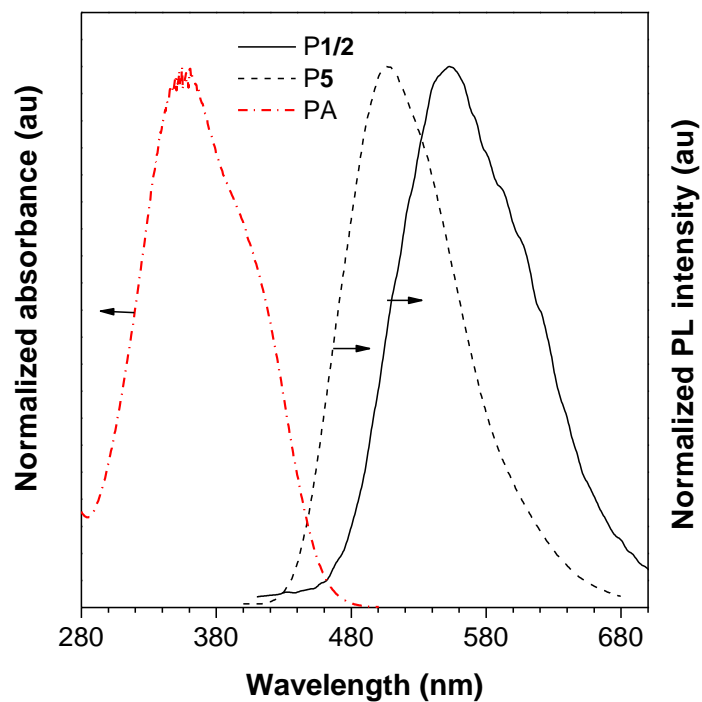


Fig. S11 UV spectrum of picric acid (PA) in water and PL spectra of P1/2 and P5 in DMF solutions at room temperature. Concentration: 10^{-5} M.

Reference

1. R. R. Hu, J. W. Y. Lam, J. Z. Liu, H. H. Y. Sung, I. D. Williams, Z. N. Yue, K. S. Wong, M. M. F. Yuen and B. Z. Tang, *Polym. Chem.*, 2012, **3**, 1481.