

Supporting Information for

A generic and effective strategy for highly effective “intrinsic” molecular luminescence in condensed state

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Instrumentation

FTIR spectra were recorded as KBr disk on a Nicolet NEXUS 8700 FTIR spectrometer. ¹H NMR spectra were collected on a Bruker DMX-400 spectrometer using chlorform-*d* (CDCl₃). Solid-state ²⁹Si NMR measurements were carried out at room temperature using a Bruker DMX-400 spectrometer at a resonance frequency of 79.49 MHz. Matrix Assisted Laser Desorption Ionization Time of Flight Mass Spectrometry (MALDI-TOF MS) was performed using a Voyager-DE RP in linear and reflectron modes. The matrix 2,5-dihydroxybenzoic acid (DHBA) was dissolved in THF (10mg/mL), and mixed with the sample solution (0.5~1 mg/mL in THF) in 1:1 v/v ratio. The samples were spotted onto the target and dried in air. The matrix 2,5-dihydroxybenzoic acid (DHBA) was dissolved in THF (10mg/mL), and mixed with the sample solution (0.5~1 mg/mL in THF) in 1:1 v/v ratio. The samples were spotted onto the target and dried in air. Elemental analyses were performed by CHNOS Elemental Analyzer, Vario El III. The optical property of the sample was measured by Shimadzu UV-265 spectrophotometer and

FP6600 Fluorescence spectrometer with a 1 cm quartz cell in tetrahydrofuran (THF, 1×10^{-5} M).

TGA was performed on a Perkin-Elmer TGA (thermogravimetric analysis) under an N_2 atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$. DSC was carried on a TA Instruments DSC 9000 equipped with a liquid nitrogen cooling accessory (LNCA) unit under a continuous nitrogen purge ($50\text{ mL}/\text{min}$). The scan rate was $10^\circ\text{C}/\text{min}$ within the temperature range $30\text{--}300^\circ\text{C}$. The atomic force microscope (AFM) images of films were taken in the tapping mode on Agilent 5500 AFM.

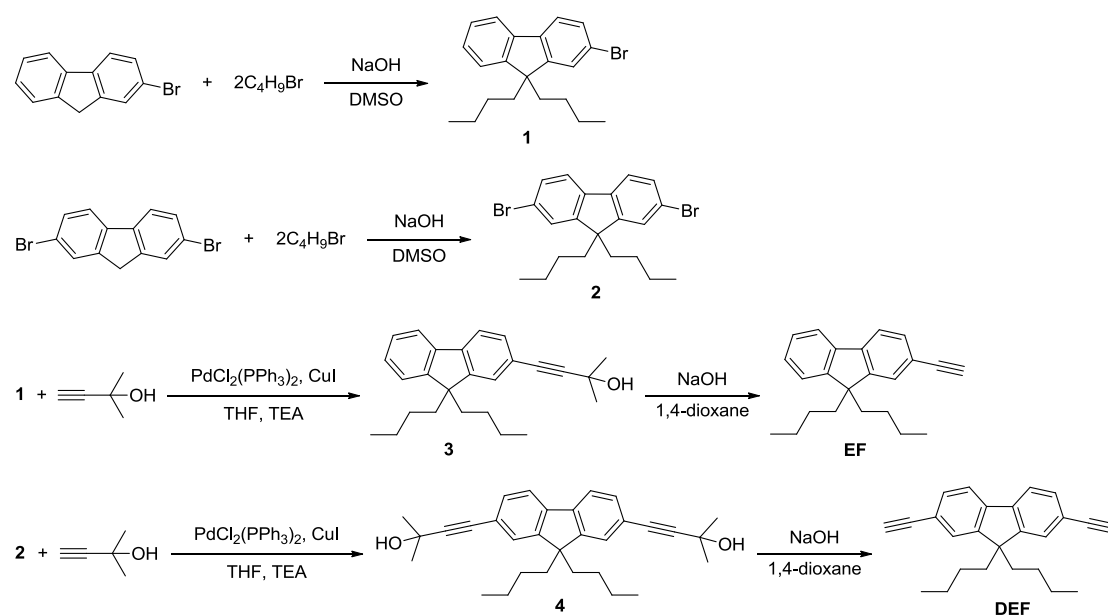
Quantum Efficiency: Photoluminescence excitation (PLE) in solution was determined by a modification of the relative method described by Demas and Crosby using 1,10-diphenylanthracene as references. The absorption at 297 nm was determined for each material at three different concentrations (maximum absorption of 20%). These samples were then diluted by equal amounts in order to avoid fluorimeter saturation and excimer formation, and the total area of the emission spectrum was calculated. For each solution, absorption and emission measurements were repeated a minimum of two times and averaged. The slope of a plot of emission versus absorption was determined for each material, and relative quantum efficiency was calculated according to the equation

$$\Phi_{\text{PL}(x)} = (A_s/A_x)(F_x/F_s)(n_x/n_s)^2 \Phi_{\text{PL}(s)} \quad (1)$$

where x is the sample to be measured, s the reference, A the absorption at the excitation wavelength, F the total integrated emission, n the refractive index of the solvent, and the quantum Φ_{PL} yield.

PLQE (Φ) of materials in film was recorded by using 9,10-diphenylanthracene (dispersed in PMMA films with a concentration lower than 1×10^{-3} M and a PLQE of 83%) as a standard.

Experimental section



Scheme S1. The synthetic route of alkynyl monomers.

2-bromo-9,9-dibutylfluorene (1): 2-dibromofluorene (4.9g, 20mmol) and tetrabutyl ammonium bromide (38mg, 0.16mmol) were dissolved in 100ml DMSO. After the reaction mixture was stirring violently, 7ml of 0.5M aqueous NaOH solution and 1-bromobutane (4.8ml, 45mmol) were added drop wise to the mixture. The reaction mixture was stirred at room temperature for 3h. A precipitate was formed by adding 500ml water and filtered off. The solid was recrystallized from n-hexane to give white crystals (95%). mp 66 °C; ^1H NMR (400 MHz, CDCl_3 , δ): 7.64-7.66 (m, 1H; Ar-H), 7.53-7.55 (d, 1H; Ar H), 7.42-7.45 (m, 2H; Ar H), 7.30-7.31 (m, 3H; Ar H), 1.90-1.95 (m, 4H; CH_2), 1.04-1.26 (m, 4H; CH_2), 0.82 (t, $J=7.1$ Hz, 6H; CH_3), 0.57-0.60 (m, 4H; CH_2); FTIR (cm^{-1} , KBr): 2927, 2854 (s; CH_2), 1462, 1112 (m; Ar). Elem. Anal. Calcd for $\text{C}_{21}\text{H}_{25}\text{Br}$: C, 70.59; H, 7.05. Found: C, 70.75; H, 6.94.

2,7-Dibromo-9,9-dibutylfluorene (2): 1-Bromobutane (3.97 g, 29.0 mmol) was added by using a syringe to a mixture of 2, 7-dibromofluorene (3.88g, 12.0mmol), tetrabutyl ammonium bromide (0.0225 g, 0.0975mmol) and 3.75 mL of 50% aqueous NaOH in DMSO (50.0 mL). The reaction

mixture was stirred at room temperature for 3h. The mixture was poured into H₂O (500 mL), and then was extracted three times with dichloromethane. The combined organic layers were dried over anhydrous MgSO₄ and decolor by active carbon. The solvent was removed under reduced pressure. The crude product was purified by recrystallization by hexane as solvent to yield a colorless crystal (90%). mp 112 °C; ¹H NMR (400MHz, CDCl₃, δ): 7.56 (d, 2H; Ar-H), 7.49 (m, 4H; Ar H), 1.96 (m, 4H; CH₂), 1.14 (m, 4H; CH₂), 0.74 (t, 6H; CH₃), 0.62 (m, 4H; CH₂); FTIR (cm⁻¹, KBr): 2950, 2868 (s; CH), 1599, 1515, 858 (m; Ar). Elem. Anal. Calcd for C₂₁H₂₄Br₂: C, 57.82; H, 5.55. Found: C, 57.52; H, 5.81.

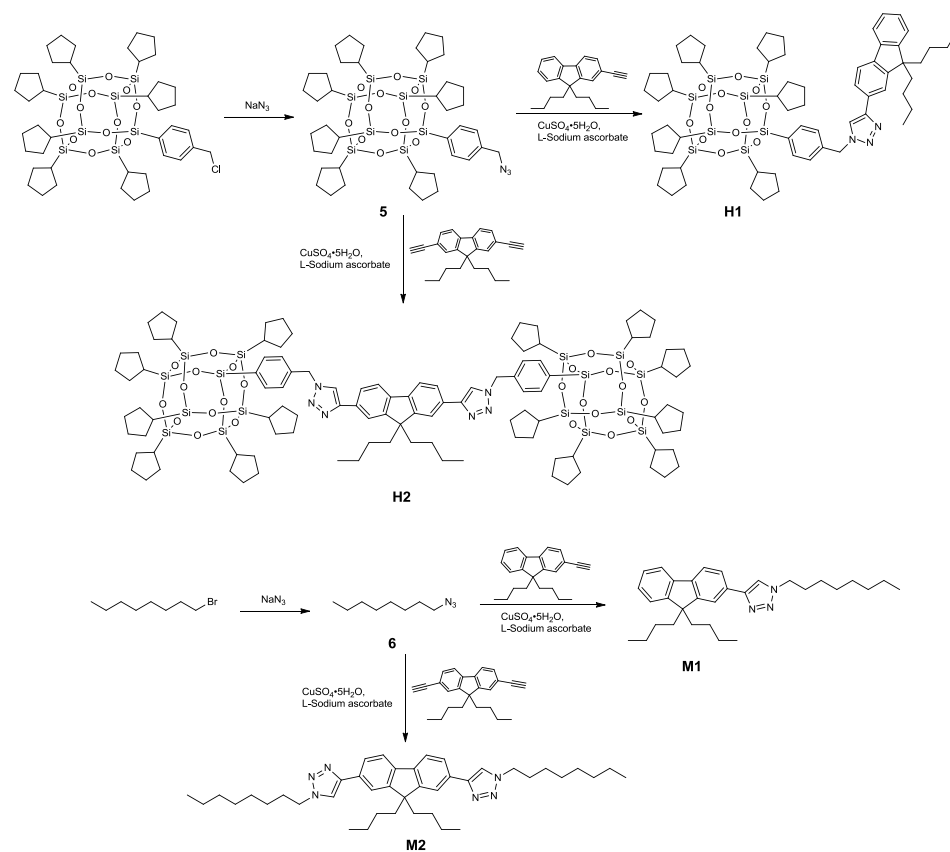
4-(9,9-dibutyl-9H-fluoren-2-yl)-2-methylbut-3-yn-2-ol (3): Under nitrogen, a mixture of compound 2-bromo-9,9-dibutylfluorene (0.18g, 0.5mmol), 2-methylbut-3-yn-2-ol (0.4ml, 4mmol), PdCl₂(PPh₃)₂ (14mg, 0.02mmol) and CuI (2mg, 0.01mmol) was dissolved in 10 ml TEA and 10ml THF. The reaction mixture was refluxed at 70 °C for 10h. After cooling to room temperature, the insolubles were filtered off. After the removal of the solvent with a rotary evaporator, water and CH₂Cl₂ were added to the mixture, and the organic phase was purified by column chromatography on silica gel with ethyl acetate/petroleum ether mixture (1:10 v/v) to give with yellow crystals (85%). mp 57 °C; ¹H NMR (400 MHz, CDCl₃, δ): 7.61-7.68 (m, 2H; Ar H), 7.39-7.41 (m, 2H; Ar H), 7.31-7.33 (m, 3H; Ar H), 2.08 (s, 1H; OH), 1.94 (t, *J*=7.7 Hz, 4H; CH), 1.66 (s, 6H; CH₃), 1.02-1.25 (m, 4H; CH₂), 0.82 (t, *J*=7.1 Hz, 6H; CH₃), 0.55-0.58 (m, 4H; CH₂); FTIR (cm⁻¹, KBr): 3378 (m; -OH), 2927, 2852 (s; -CH₂), 2228 (w; C≡C), 1458, 1166 (m; Ar-H). Elem. Anal. Calcd for C₂₆H₃₂O: C, 86.62; H, 8.95. Found: C, 86.81; H, 8.73.

2-ethynyl-9,9-dibutylfluorene (EF): Under nitrogen, a mixture of compound 2-(2-methyl-3-butyne-2-ol)-9,9-dibutylfluorene (0.1g, 0.25mmol), NaOH (4.8g, 1.2mmol) was

added into 20ml 1,4-dioxane. The reaction mixture was refluxed at 80 °C for 4h. After cooling to room temperature, water and CH₂Cl₂ were added to the mixture, and the organic phase purified by column chromatography on silica gel with ethyl acetate/petroleum ether mixture (1:6 v/v) to give with yellow crystals (95%). mp 70 °C; ¹H NMR (400 MHz, CDCl₃, δ): 7.66-7.74 (m, 2H; Ar H), 7.51-7.53 (m, 2H; Ar H), 7.32-7.39 (m, 3H; Ar H), 3.16 (s, 1H; C≡CH), 1.97-2.02 (m, 4H; CH₂), 1.08-1.32 (m, 4H; CH₂), 0.86 (t, *J*=7.1 Hz, 6H; CH₃), 0.59-0.69 (m, 4H; CH₂); FTIR (cm⁻¹, KBr): 3275 (s; C≡C-H), 2954, 2924, 2854 (s; -CH₂), 2099 (w; C≡C), 1451, 1126 (m; Ar-H). Elem. Anal. Calcd for C₂₃H₂₆: C, 91.34; H, 8.66. Found: C, 91.11; H, 8.89.

4,4'-(9,9-dibutyl-9H-fluorene-2,7-diyl)bis(2-methylbut-3-yn-2-ol) (4): This was prepared as above **3**. Yield: 70%. mp 103 °C; ¹H NMR (400 MHz, CDCl₃, δ): 7.60(d, *J* = 7.7 Hz, 2H; Ar H), 7.38(m, 4H, Ar H), 2.03(s, 2H, OH), 1.92(m, *J* = 4.2 Hz, 4H; CH₂), 1.27-1.02(m, 4H; CH₂), 0.87(t, *J* = 7.2 Hz, 6H; CH₃), 1.65(s, 12H; CH₃), 0.54(m, *J* = 4.0 Hz, 4H; CH₂). FTIR (cm⁻¹, KBr): 3350(OH), 2926(CH₃), 2853(CH₂), 2222(C≡C), 1639, 887(Ar). Elem. Anal. Calcd for C₃₁H₃₈O₂: C, 84.12; H, 8.65. Found: C, 84.01; H, 8.72.

2,7-diethynyl-9,9-dibutylfluorene (DEF): This was prepared as above **4**. Yield: 80%. mp 114 °C; ¹H NMR (400 MHz, CDCl₃, δ): 7.62(d, *J* = 7.6 Hz, 2H; Ar H), 7.46(t, *J* = 5.6 Hz, 4H; Ar H), 3.13(2H, s, C≡C-H), 1.93(4H, m, CH₂), 1.27-1.02(4H, m, CH₂), 0.86(6H, t, *J* = 6.9 Hz, CH₃), 0.57(d, *J* = 7.2 Hz, 4H; CH₂). FTIR (cm⁻¹, KBr): 3309(C≡C-H), 2920(CH₃), 2853(CH₂), 2106(C≡CH), 1639, 887(Ar). Elem. Anal. Calcd for C₂₅H₂₆: C, 91.97; H, 8.03. Found: C, 91.91; H, 8.09.



Scheme S2. The synthetic route of H1, H2, M1 and M2.

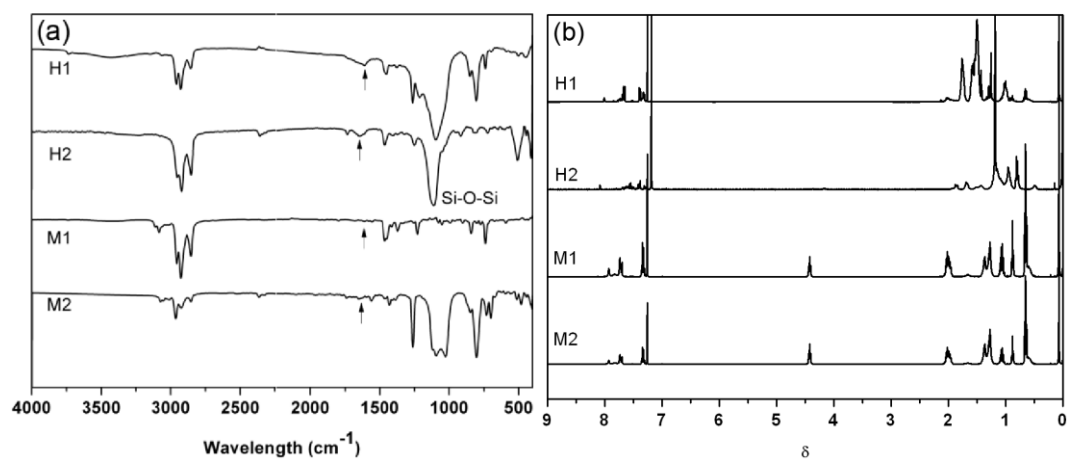


Fig. S1 The FTIR (a) and ^1H NMR (b) spectra of M1, M2, H1 and H2

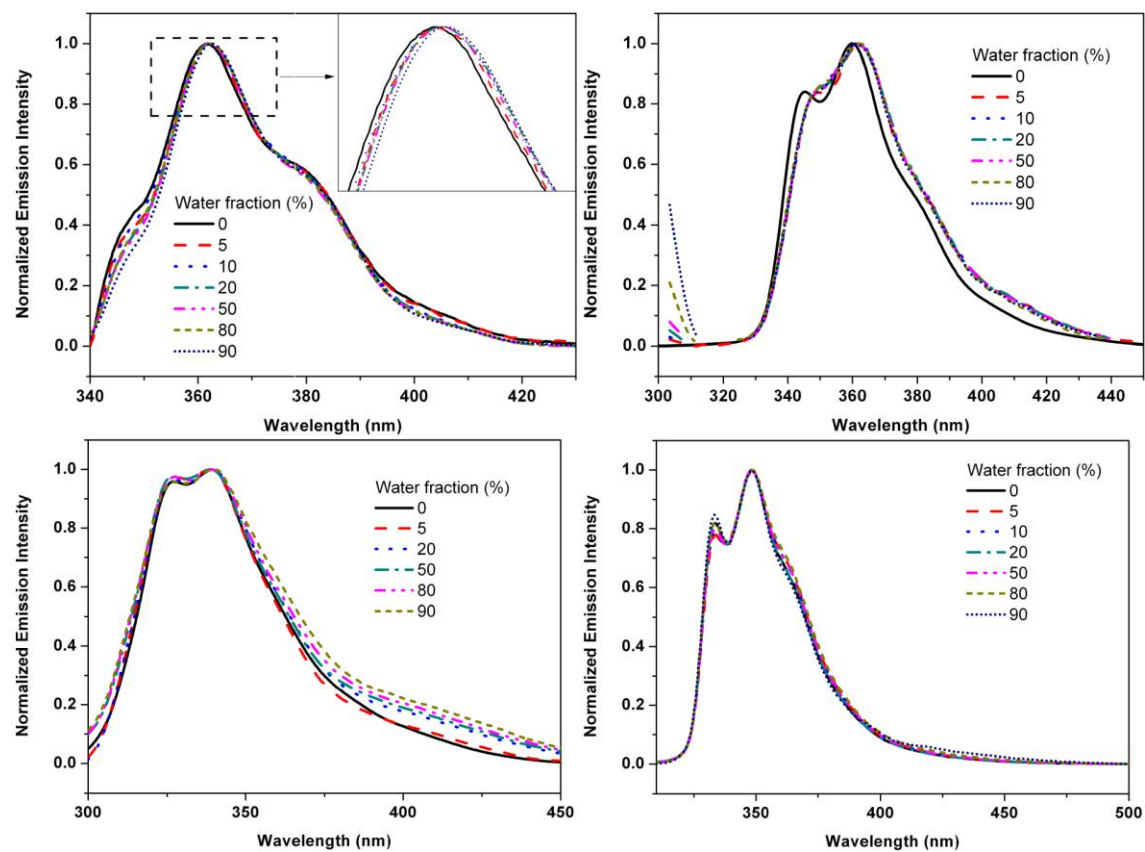


Fig. S2 Normalized PL spectra of the dilute solutions of M1(a), M2(b), H1(c), and H2(d) (10^{-6} mol/L) in THF/Water mixtures with different water contents.

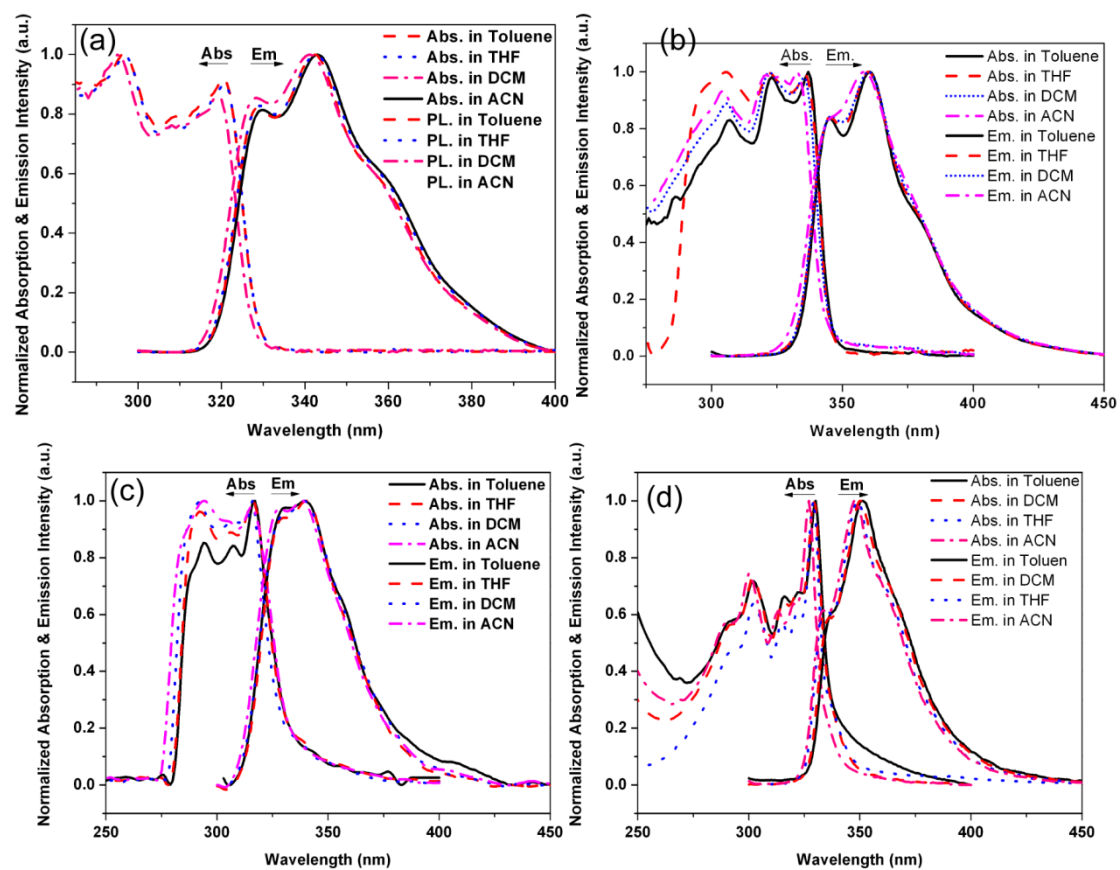


Fig. S3 Solvatochromism of **M1**(a), **M2**(b), **H1**(c) and **H2**(d) in Toluene, THF, DCM and ACN.

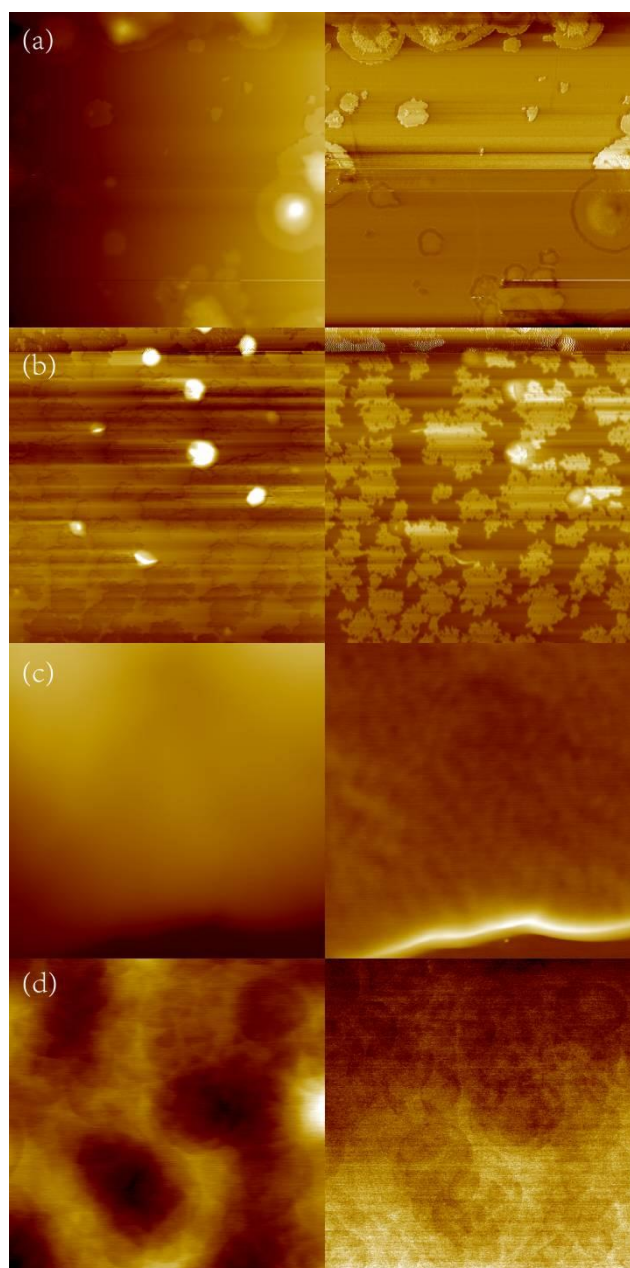


Fig. S4 Atomic force microscope images of $9 \times 9 \mu\text{m}^2$ tapping mode for M1 (a), M2 (b), H1 (c) and H2 (d) films: (left) height and (right) phase images (Z ranges for the height and phase images are 33, 28, 8, 6 nm, respectively)

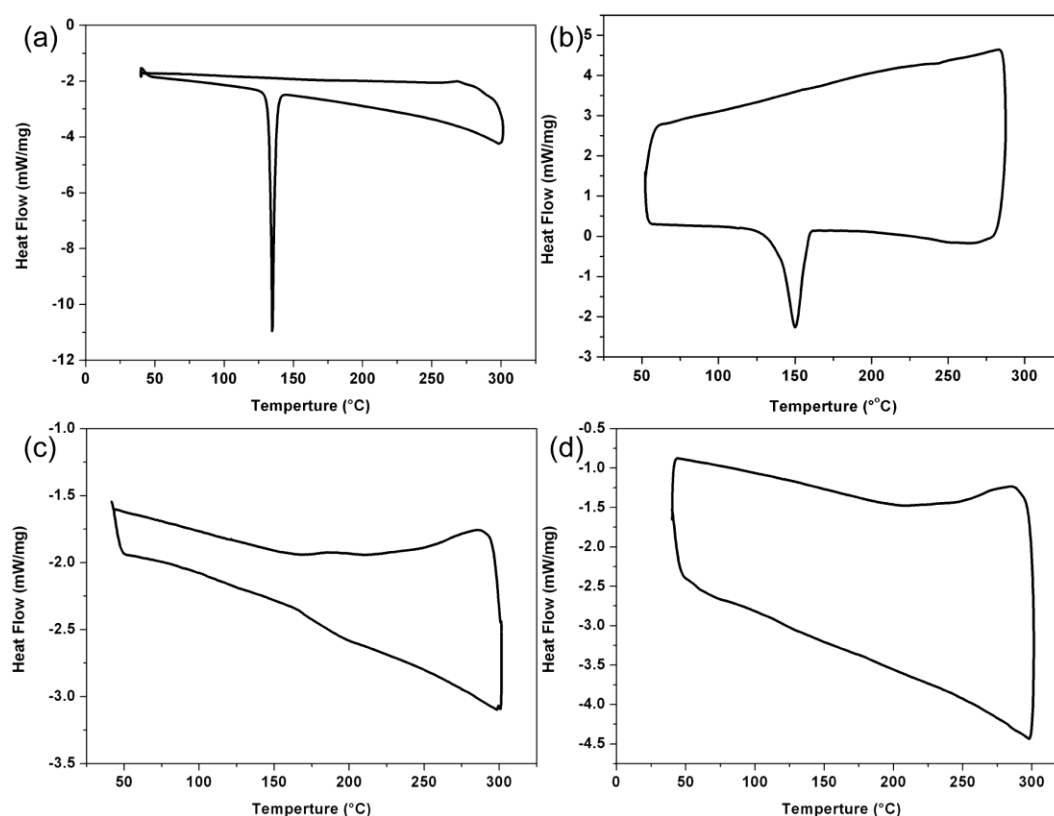


Fig. S5 DSC curve of **M1**(a), **M2**(b), **H1**(c) and **H2**(d)

Table S1 Absorption and emission maxima (nm)^a of **M1**, **M2**, **H1** and **H2** in a series of solvents.

Solvent	M1		M2		H1		H2	
	λ_{abs}	λ_{em}	λ_{abs}	λ_{em}	λ_{abs}	λ_{em}	λ_{abs}	λ_{em}
Toluene	298,321	343	330	351	294,317	337	330	350
Tetrahydrofuran	297,320	342	329	350	293,316	339	329	350
Dichloromethane	297,321	343	329	349	292,316	338	329	349
Acetonitrile	295,319	341	327	348	294,316	337	330	350

^a In THF (10^{-5} mol/L). Excitation wavelength was 297 nm.

Table S2 Thermal characterization of compounds.

compound	T _g (°C)	T _m (°C)	T _{d5%} (°C)	ceramic yield, %	theor yield, %
AF	-	-	156.8	8.1	-
POSSCl	-	-	349.3	39.7	40.6
M1	-	134.5	335.9	3.61	-
M2	115.5	167.6	260.5	2.82	-
H1	-	-	380.2	45.0	45.9
H2	-	149.2	394.6	26.5	52.8