Supproting Information

Pure White Light Emission and Charge Transfer In Organogels of Symmetrical and Unsymmetrical π-Chromophoric *Oligo-p*-(phenyleneethynylene) Bola-amphiphiles

Syamantak Roy,† Debabrata Samanta,† Pramod Kumar, and Tapas Kumar Maji*

Molecular Materials Laboratory, Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore-560064, India
E-mail: tmaji@jncasr.ac.in; Tel: +91-8022082826
† Authors contributed equally.

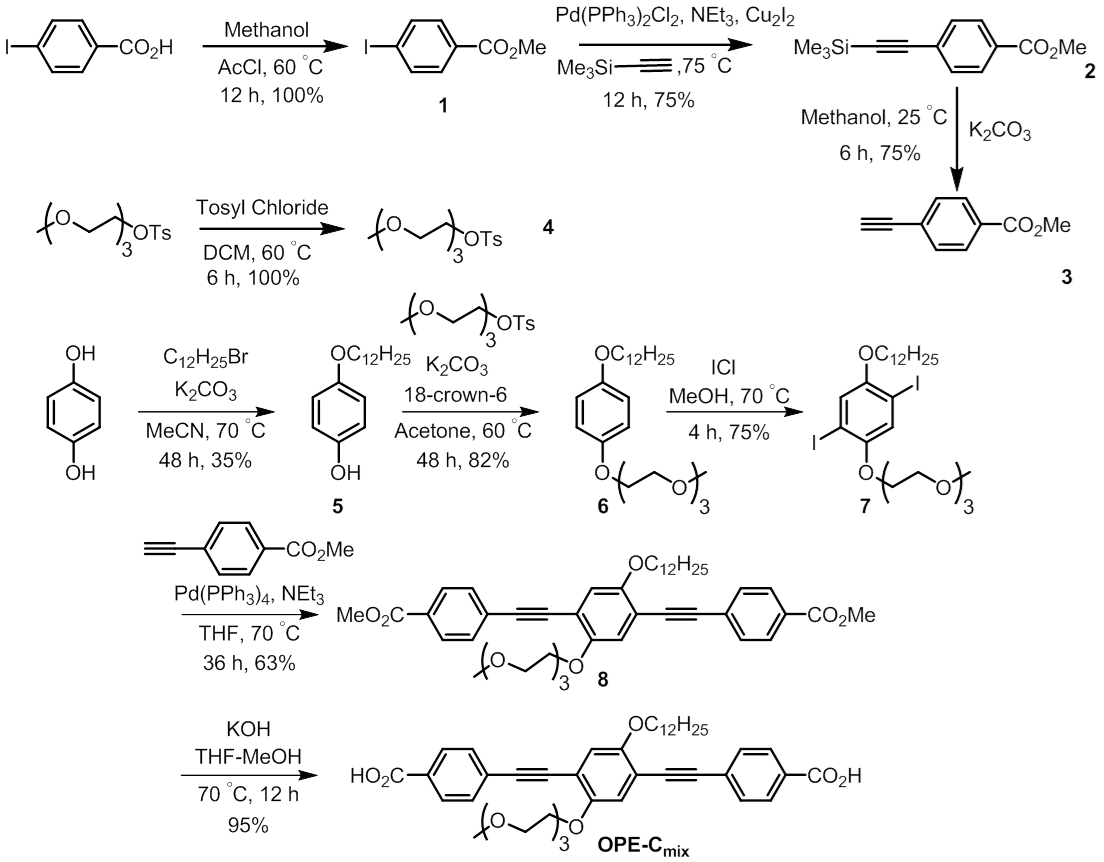
Contents

Experimental Section
Materials and Methods:

$Pd(PPh_3)_4$, hydroquinone and methyl-4-iodobenzoate were purchased from Sigma-Aldrich chemical Co. Ltd. Cuprous iodide was obtained from Loba Chemie Pvt. Ltd. Solvents were pre-dried using standard literature procedures. Fourier transform infrared (FTIR) spectra were recorded by making samples with KBr pellets using Bruker FT-IR spectrometer. UV-Vis spectra were recorded in a Perkin-Elmer lamda 900 spectrometer. UV-Vis experiments were carried out with spectroscopic grade solvents purchased from Spectrochem Ltd. ^1H and ^{13}C NMR spectrum are recorded on a Bruker AV-400 spectrometer with chemical shifts recorded as ppm and all spectra were calibrated against TMS. Fluorescence measurements were accomplished using Perkin Elmer Ls 55 Luminescence spectrometer. The solid state fluorescence quantum yield of solid powder and xerogel was determined by using integrating sphere, an absolute quantum yield measurement and calculated by Horiba Jobin Yvon. Lifetime measurements were carried out on an EPL-405 ps pulsed diode laser (Edinburgh instrument) used as the excitation source (λ_{ex}= 404 nm). Powder X-ray diffraction measurements were carried out on a Bruker D8 discover instrument using Cu-Kα radiation. Elemental analyses were carried out using a Thermo Scientific Flash 2000 CHN analyzer. Morphology studies were performed using Lica-S440I field emission scanning electron microscopy (FESEM) by placing samples on silicon wafer under vacuum with an accelerating voltage of 10 kV. Transmission electron microscopy (TEM) studies were done on JEOL JEM-3010 with accelerating voltage of 300 kV.

Synthetis and characterization for OPE-C_{12} and OPE-C_{mix}

General procedure and characterization. Chemical shifts (δ) are indicated in ppm. The following abbreviations were used to illustrate NMR signals: s = singlet, d = doublet, t = triplet, td = triplet of doublets, dd = doublet of doublets, ddd = doublet of doublets of doublets, m = multiplet. Methyl 4-ethynylbenzoate[1] 2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate,[2] 4-(dodecyloxy)phenol[3] and 4,4'-((2,5-bis(dodecyloxy)-1,4-phenylene)bis(ethyne-2,1-diyl))dibenzoic acid[4] were prepared according to reported procedures. OPE-C_{12} was synthesized according to reported procedures.[4,5]



Scheme S1. Synthetic scheme for OPE-C_{mix}.

Synthesis of 1-(dodecyloxy)-4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene (6). Solid K_2CO_3 (4.70 g, 33.8 mmol) was added portion wise to a stirring solution of 4-

(dodecyloxy)phenol (**1**) (4.70 g, 16.9 mmol), 2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate (5.85 g, 16.9 mmol) and 18-crown-6 (446 mg, 1.69 mmol) in 50 mL acetone. The solution was refluxed at 60 °C for 2 days to complete the reaction. The reaction mixture was filtered to remove excess K_2CO_3 and the filtrate was concentrated under rotary evaporator. The crude product was purified by column chromatography (silica gel, hexane/ethyl acetate = 10:1) yielding 1-(dodecyloxy)-4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene (**2**) as white solid (7.12 g, 16.8 mmol, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.88 (t, *J* = 6.8 Hz, 3H), 1.27-1.37 (m, 16H), 1.49 (q, *J* = 7.2 Hz, 2H), 1.80 (q, *J* = 8.0 Hz, 2H), 3.38 (s, 3H), 3.54-3.57 (m, 2H),), 3.66-3.70 (m, 4H), 3.77-3.80 (m, 2H), 3.87 (t, *J* = 4.4 Hz, 2H), 3.92 (t, *J* = 6.4 Hz, 2H), 4.10 (t, *J* = 5.2 Hz, 2H), 7.16-7.17 (m, 2H), 7.24-7.15 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.3, 22.8, 26.2, 29.5, 29.6, 29.6, 29.8, 29.8, 29.8, 29.8, 32.1, 59.2, 68.3, 68.8, 70.1, 70.7, 70.8, 71.0, 72.1, 115.6, 115.8, 153.0, 153.7 ppm. HRMS-EI (*m/z*) for $C_{25}H_{44}O_5$ [M+] Calcd. 424.319, found 424.318. Anal. Calcd. for $C_{25}H_{44}O_5$: C, 70.72; H, 10.44. Found: C, 70.97; H, 10.15.

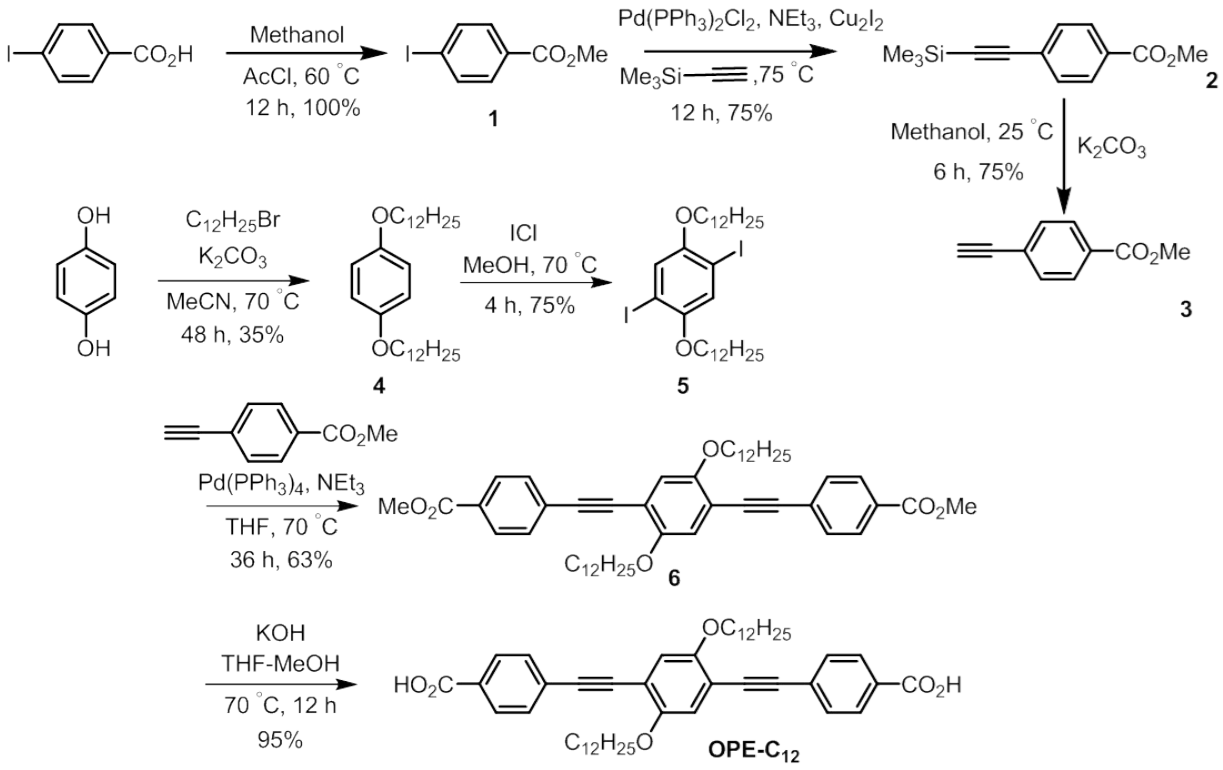
Synthesis of 1-(dodecyloxy)-2,5-diiodo-4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene (7). A solution of 1-(dodecyloxy)-4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene (**2**) (6.00g, 14.1 mmol) in 30 mL methanol was added dropwise to a stirring solution of iodine monochloride (9.18 g, 56.5 mmol) in 100 mL methanol at 0 °C. The resulting reaction mixture was refluxed overnight to complete the iodination process. The reaction mixture was cooled down to 0 °C and, then, excess iodine monochloride was quenched by addition of saturated aqueous solution of sodium thiosulfate. The crude product was extracted by dichloromethane (5×50 mL), dried over $MgSO_4$ and concentrated by rotary evaporator. The crude product was chromatographed (silica gel, hexane/ethyl acetate = 15:1) to get 1-(dodecyloxy)-2,5-diiodo-4-(2-(2-(2-

methoxyethoxy)ethoxy)ethoxy)benzene (**7**) as white solid (8.79 g, 13.0 mmol, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.88 (t, *J* = 6.9 Hz, 3H), 1.27-1.37 (m, 16H), 1.49 (q, *J* = 7.8 Hz, 2H), 1.80 (q, *J* = 6.4 Hz, 2H), 3.38 (s, 3H), 3.54-3.57 (m, 2H), 3.66-3.70 (m, 4H), 3.77-3.80 (m, 2H), 3.89 – 3.86 (m, 2H), 3.93 (t, *J* = 6.4 Hz, 2H), 4.12 – 4.08 (m, 2H), 7.16 (s, 1H), 7.25 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.3, 22.9, 26.2, 29.3, 29.4, 29.5, 29.7, 29.7, 29.8, 29.8, 32.1, 59.2, 69.8, 70.5, 70.6, 70.8, 71.0, 71.3, 72.2, 86.4, 86.7, 122.8, 123.9, 153.0, 153.5 ppm. HRMS-EI (*m/z*) for $C_{25}H_{42}I_2O_5$ [M+] Calcd. 676.112, found 676.112. Anal. Calcd. for $C_{25}H_{42}I_2O_5$: C, 44.39; H, 6.26. Found: C, 44.07; H, 6.18.

Synthesis of dimethyl 4,4'-((2-(dodecyloxy)-5-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-1,4-phenylene)bis(ethyne-2,1-diyl))dibenzoate (8). A 250 mL three-neck round-bottomed flask, charged with 1-(dodecyloxy)-2,5-diiodo-4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene (**7**) (1.00 g, 1.48 mmol), methyl 4-ethynylbenzoate (**4**) (1.18 g, 7.39 mmol), 25 mL tetrahydrofuran and 10 mL triethylamine, was degassed by freeze-pump-thaw procedure (three times). The $Pd(PPh_3)_4$ (340 mg, 296 μmol) was added to it. The resulting reaction mixture was refluxed at 70 °C for 48 h under inert atmosphere for completion of the coupling reaction. The resulting solution was concentrated and purified by column chromatography (silica gel, dichloromethane/ethyl acetate = 98:2) to obtain dimethyl 4,4'-((2-(dodecyloxy)-5-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-1,4-phenylene)bis(ethyne-2,1-diyl))dibenzoate (**8**) (0.67 g, 904 μmol, 61% yield) as greenish-yellow solid compound. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.87 (t, *J* = 6.9 Hz, 1H), 1.24-1.42 (m, 16H), 1.50-1.60 (m, 2H), 1.86 (q, *J* = 7.8 Hz, 2H), 3.50-3.53 (m, 2H), 3.61-3.67 (m, 4H), 3.80-3.82 (m, 2H), 3.92-3.94 (m, 8H), 4.04 (t, *J* = 6.4 Hz, 2H), 4.22 (t, *J* = 5.2 Hz, 2H), 7.02 (s, 1H), 7.06 (s, 1H), 7.59 (d, *J* = 7.7 Hz, 2H), 8.03 (d, *J* = 8.4 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.3, 22.8, 26.3, 29.5, 29.5, 29.6, 29.8, 29.8, 29.8, 29.9, 32.1,

52.4, 52.4, 59.2, 69.8, 70.0, 70.7, 70.9, 71.3, 72.1, 89.0, 94.5, 114.2, 117.1, 117.7, 128.2, 129.7, 129.7, 129.8, 131.6, 153.6, 154.3, 166.7 ppm. HRMS-EI (*m/z*) for $C_{45}H_{56}O_9$ [M+] Calcd. 740.392, found 740.395. Anal. Calcd. for $C_{45}H_{56}O_9$: C, 72.95; H, 7.62. Found: C, 72.89; H, 7.49.

Synthesis of 4,4'-((2-(dodecyloxy)-5-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-1,4-phenylene)bis(ethyne-2,1-diyl))dibenzoic acid (OPE-C_{mix}). K_2CO_3 flakes (1.00 g, 7.25 mmol) was added to a solution of 4,4'-((2-(dodecyloxy)-5-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-1,4-phenylene)bis(ethyne-2,1-diyl))dibenzoate (**8**) (500 mg, 675 μmol) in 40 mL methanol. The resulting solution was refluxed for 12 h at 70 °C to complete ester hydrolysis. The clear solution was added dropwise over 4 N aq. HCl solution (250 mL) and greenish-yellow precipitate of 4,4'-((2-(dodecyloxy)-5-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-1,4-phenylene)bis(ethyne-2,1-diyl))dibenzoic acid (**9**) was formed which was filtered off and washed with water (100 mL) and methanol (25 mL, caution: slightly soluble) to get pure compound (420 mg, 589 μmol, 87% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 0.83 (t, *J* = 6.9 Hz, 1H), 1.12-1.23 (m, 14H), 1.30-1.40 (m, 2H), 1.50 (q, *J* = 8.0 Hz, 2H), 1.50 (q, *J* = 8.0 Hz, 2H), 1.75 (q, *J* = 7.8 Hz, 2H), 3.19 (s, 3H), 3.47-3.53 (m, 6H), 3.66-3.69 (m, 2H), 3.80 (t, *J* = 4.4 Hz, 2H), 4.07 (t, *J* = 6.0 Hz, 2H), 4.20 (t, *J* = 4.4 Hz, 2H), 7.23 (s, 1H), 7.25 (s, 1H), 7.60-7.65 (m, 4H), 7.97-7.99 (m, 4H), 13.1 (br, H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, DMSO-d^6) δ = 13.8, 22.3, 25.7, 29.0 (2C), 29.1, 29.3, 29.3, 29.3, 29.3, 31.6, 58.6, 69.3, 69.4, 69.5, 70.2, 70.4, 70.8, 71.6, 88.3, 94.3, 113.7, 113.9, 116.7, 117.3, 127.3, 129.4, 130.3, 131.0, 153.1, 153.8, 167.5 ppm. HRMS-EI (*m/z*) for $C_{43}H_{52}O_9$ [M+] Calcd. 712.361, found 712.360. Anal. Calcd. for $C_{43}H_{52}O_9$: C, 72.45; H, 7.35. Found: C, 72.40; H, 7.19.



Scheme S2 Synthetic scheme of OPE-C_{12}.

OPE-C_{12} was synthesized according to reported procedures.[4.5]

Gelation of OPE-C_{12} and OPE-C_{mix}

10 mg of OPE-C_{12} and OPE-C_{mix} were dissolved in 0.25 mL of ethylacetate at 333 K. This was followed by the addition of 0.75 mL of toluene while constantly shaking the vial. The solution was allowed for stand for 1 min after which it entirely converted into a stable gel phase. The formed gels were dissolved at 333 K to form the sol state and again reverted back to the gel state thus proving their thermoreversibility.

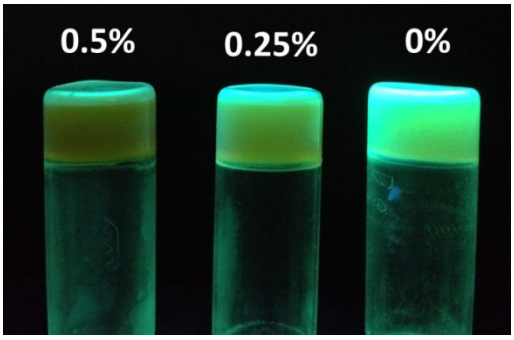
Preparation of gel with methyl red (MR) dye

10 mol% of MR was dissolved in ethyl acetate along with OPE-C_{mix}-G at 60 ^{0}C. Toluene was added dropwise to the mixture and allowed to stand for 5 mins when an orange colored gel formed (MR10@ OPE-C_{mix}-G). Mixed gels of other concentrations (1, 2 annd 5) mol% were also prepared following the above procedure.

Image of OPE-C_{mix}-G after the incorporation of methyl red

Preparation of OPE-C_{mix} gel with TCNQ

0.25 mol% TCNQ was dissolved in ethyl acetate along with OPE-C_{mix}-G at 60 ºC. Toluene was added dropwise to the mixture and allowed to stand for 5 mins when a dark green colored gel formed ($TCNQ_{0.5}$@OPE-C_{mix}-G). $TCNQ_{0.25}$@OPE-C_{mix}-G was also prepared following the above procedure.



Images of OPE-C_{mix}-G, $TCNQ_{0.25}$@OPE-C_{mix}-G and $TCNQ_{0.5}$@OPE-C_{mix}-G under UV light (left to right)

Tabulation of solvent mixtures used for gelation

Table S1. Tabulation of the solvent ratios in which OPE-C_{12} and OPE-C_{mix} gels are prepared.

	Toluene/EtOAc 3:1	Benzene/EtOAc 3:1	Cyclohexane/EtOAc 3:1	Hexane/EtOAc 3:1
OPE-C_{12}	Yes	Yes	Yes	Yes
OPE-C_{mix}	Yes	Yes	Yes	Yes

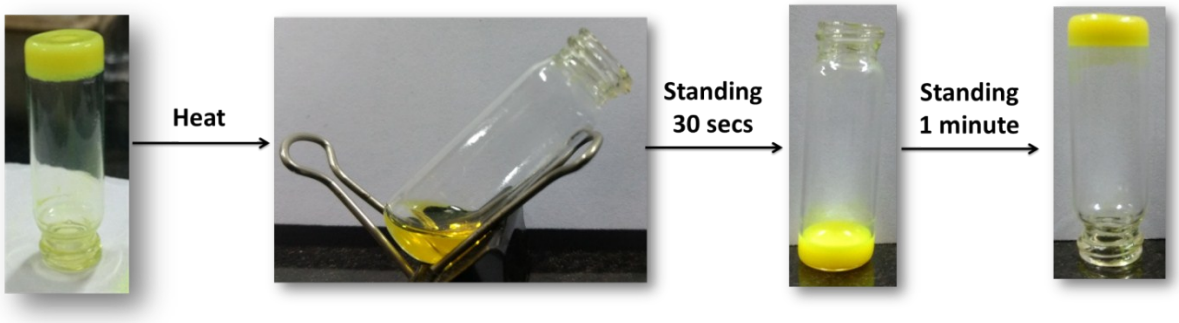


Fig. S1 Images of the thermoreversibility test performed on OPE-C_{mix}.

PXRD profile of gels

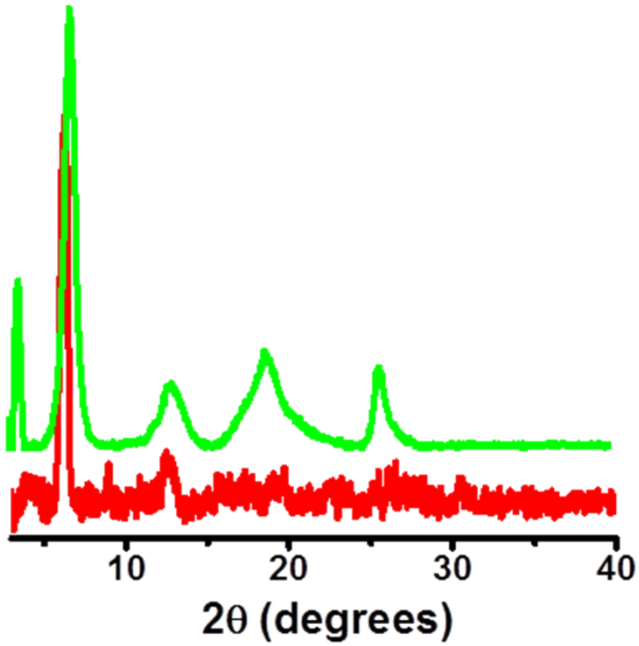


Fig. S2 PXRD of OPE-C_{12}-G (red) and OPE-C_{mix}-G (green) xerogels.

FESEM images of gels

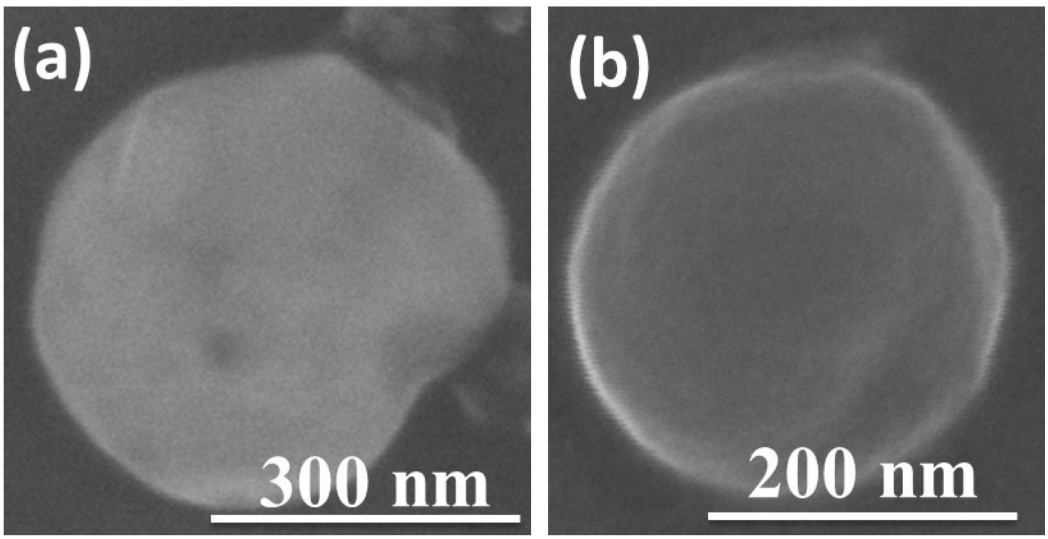


Fig. S3 FESEM images of (a) OPE-C_{12}-G and (b) OPE-C_{mix}-G

Water Contact Angle Measurement

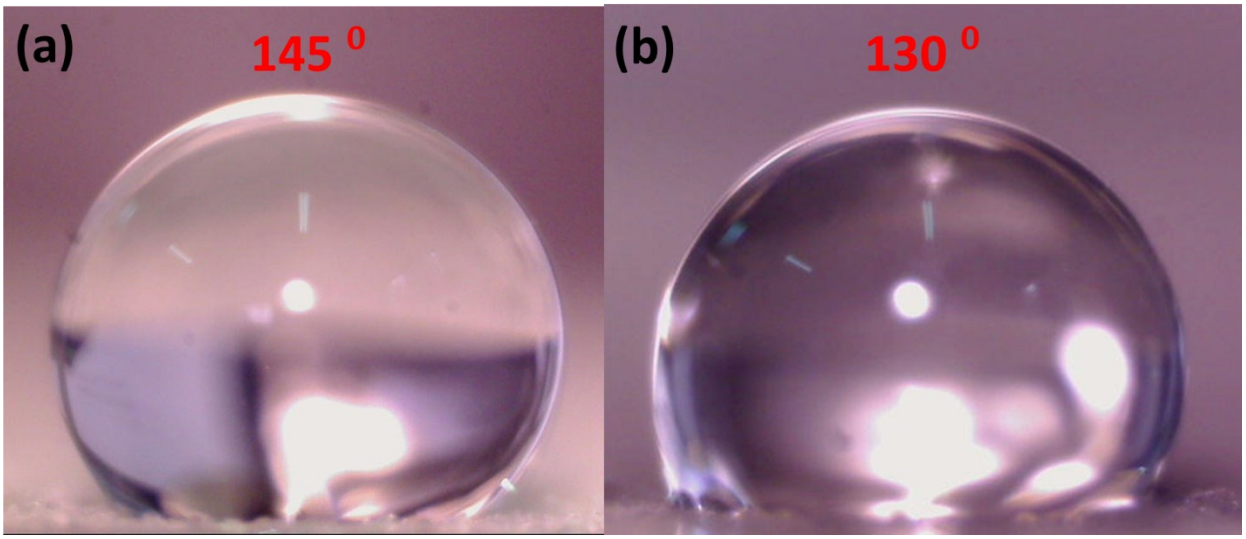


Fig. S4 Contact angles of a 5μL water droplet on glass surfaces coated with (a) OPE-C_{12}-G and (b) OPE-C_{mix}-G xereogels.

Solution state UV and PL

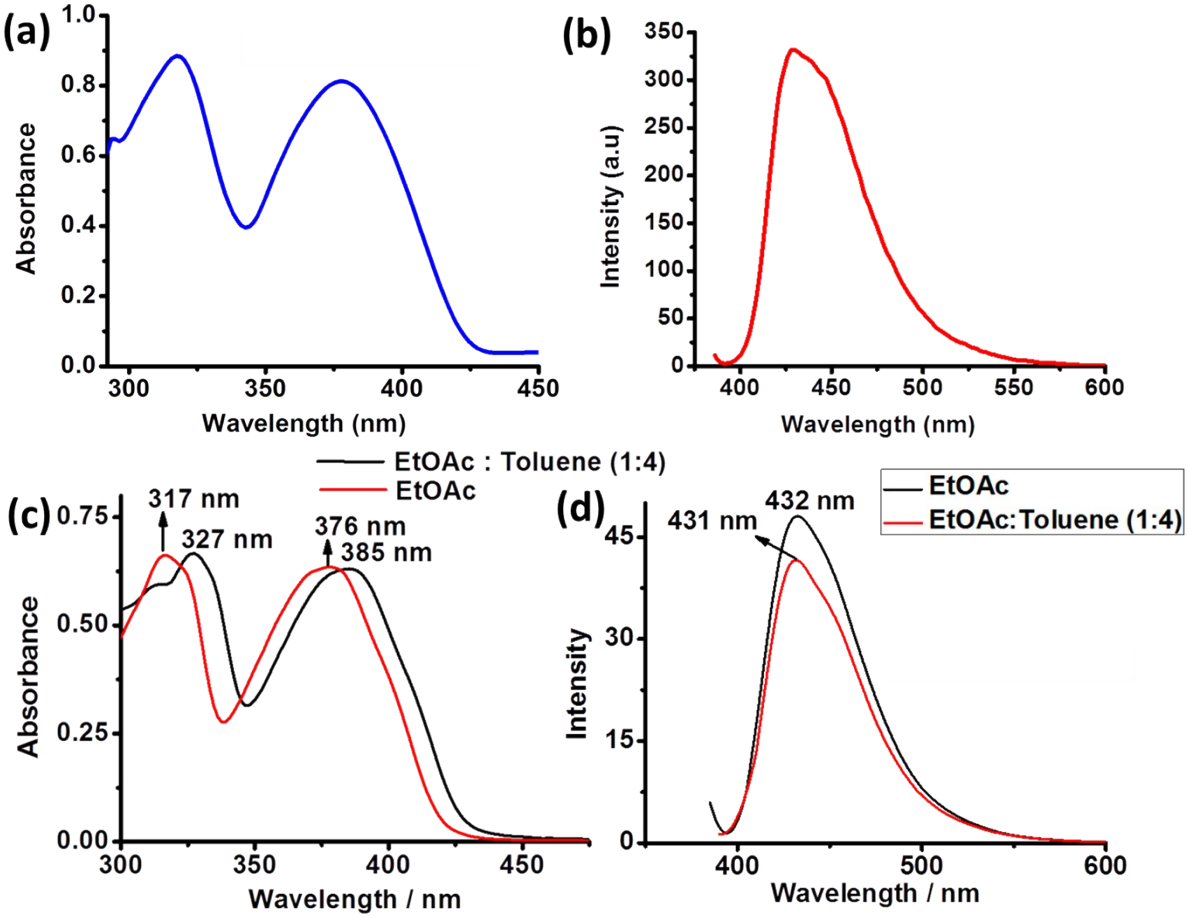


Fig. S5 (a,c) UV-Vis spectra for OPE-C_{12} and OPE-C_{mix} respectively in a ethyl acetate/toluene mixture, (b,d) emisison spectra for OPE-C_{12} and OPE-C_{mix} in a ethyl acetate (black) and ethyl acetate/toluene (red) mixture.

Solid state UV spectra of ligands

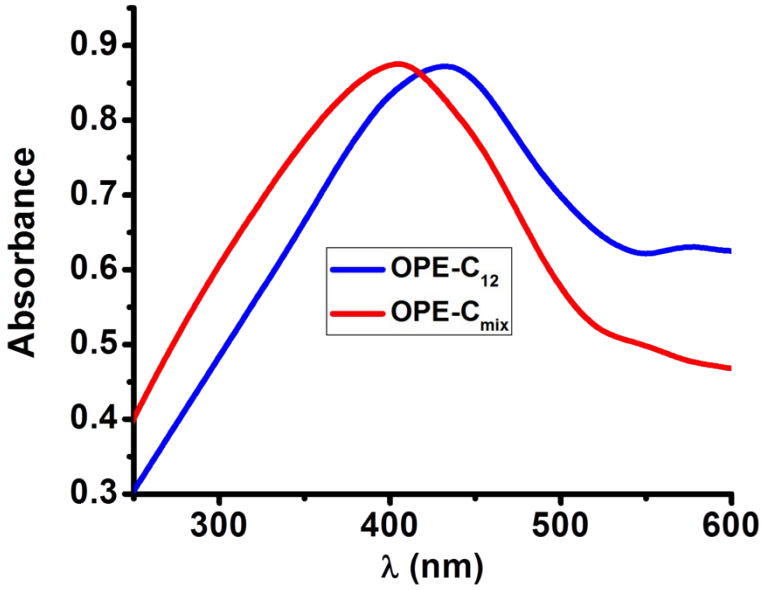


Fig. S6 Solid state UV spectra of (a) OPE-C_{12} (blue) and (b) OPE-C_{mix} (red).

Solid state emission spectra of ligands

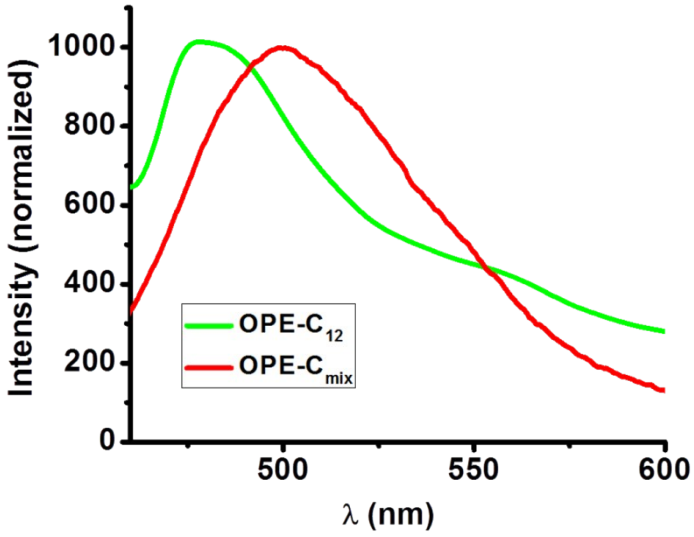


Fig. S7 Solid state emission spectra of (a) OPE-C_{12} (green) and (b) OPE-C_{mix} (red). (λ_{ex}=380 nm).

Solid state UV spectra of gels

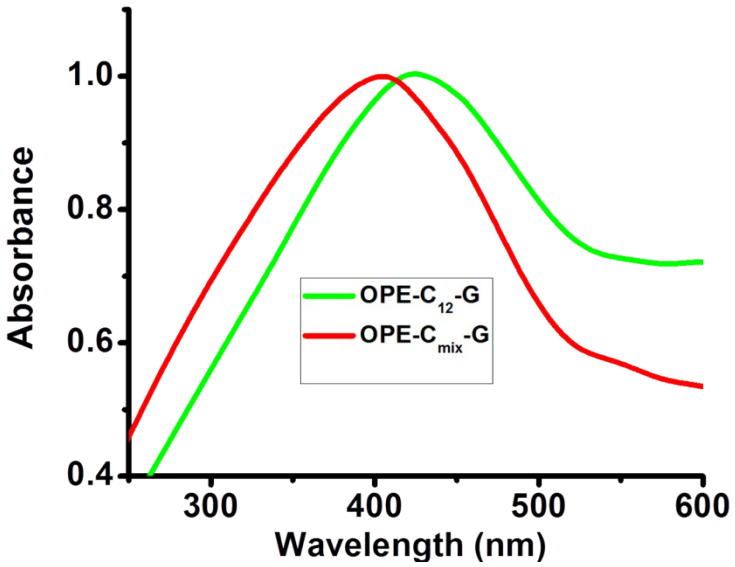


Fig. S8 Solid state UV spectra of (a) OPE-C_{12}-G (green) and (b) OPE-C_{mix}-G (red) xerogels.

Excitation Spectra of methyl red incorporated gel

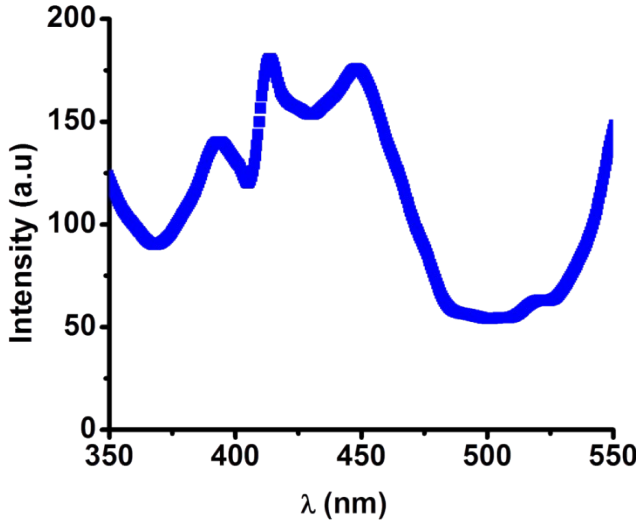


Fig. S9 Excitation spectra of MR10@OPE-C_{mix}-G monitored at 590 nm.

Time-resolved fluorescence decay profiles of gels

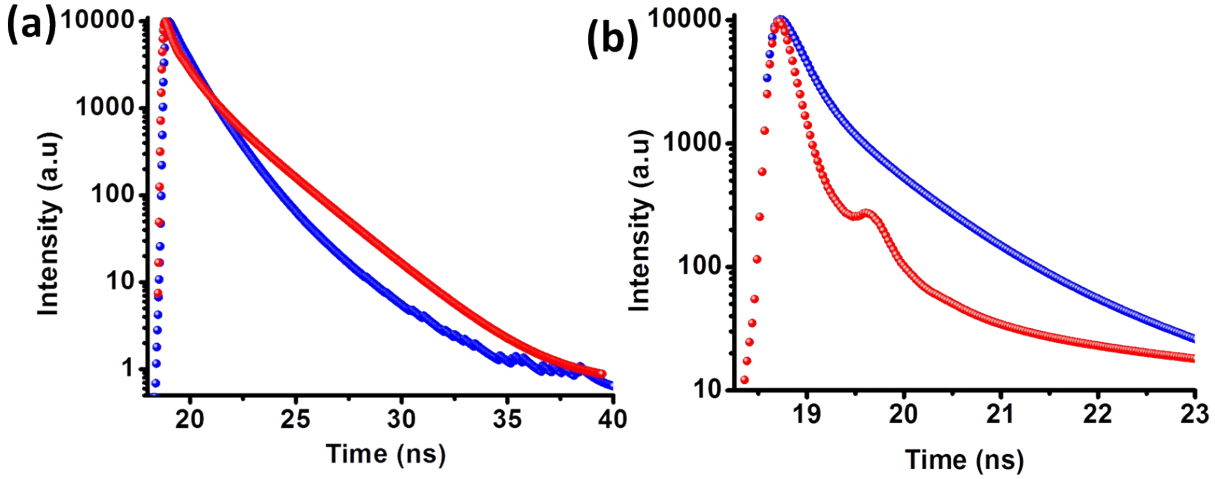


Fig. S10 Lifetime decay profiles for (a) OPE-C_{mix}-G (red) and MR10@OPE-C_{mix}-G (blue) monitored at 485 nm and (b) MR (red) and MR10@OPE-C_{mix}-G (blue) monitored at 590 nm.

Emission spectra of different loading concentrations of MR@OPE-C_{mix}-G

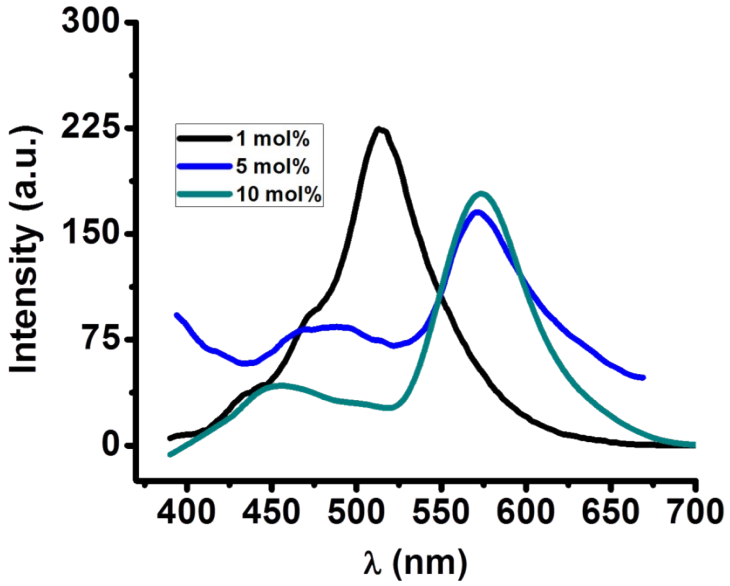


Fig. S11 Emission plots (λ_{ex}= 380 nm) of pure OPE-C_{mix}-G and MR@OPE-C_{mix}-G at different loading concentrations of MR.

References

1 N. V. Harris, S. Christopher and B. Keith, *Synlett*, 1990, 577.

2 S. Chakraborty, S. G. Ramkumar, S. Ramakrishnan, *Macromolecules*, 2017, **50**, 5004.

3 P. K. Lo and H. F. Sleiman, *J. Am. Chem. Soc*., 2009, **131**, 4182.

4 M. Sankarapillai, T. Rajasekaran, Y. Shiki, K. Akihide and A. Ayyappanpillai, *Chem. Commun*., 2009, **40**, 5984.

5 S. Roy, M. Das, A. Bandyopadhyay, S. K. Pati, P. P. Ray and T. K. Maji, *J. Phys. Chem. C*, 2017, **121**, 23803.