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Supporting Information for

Solvent Assisted Fluorescence Modulation of a C_3 - Symmetric Organogelator

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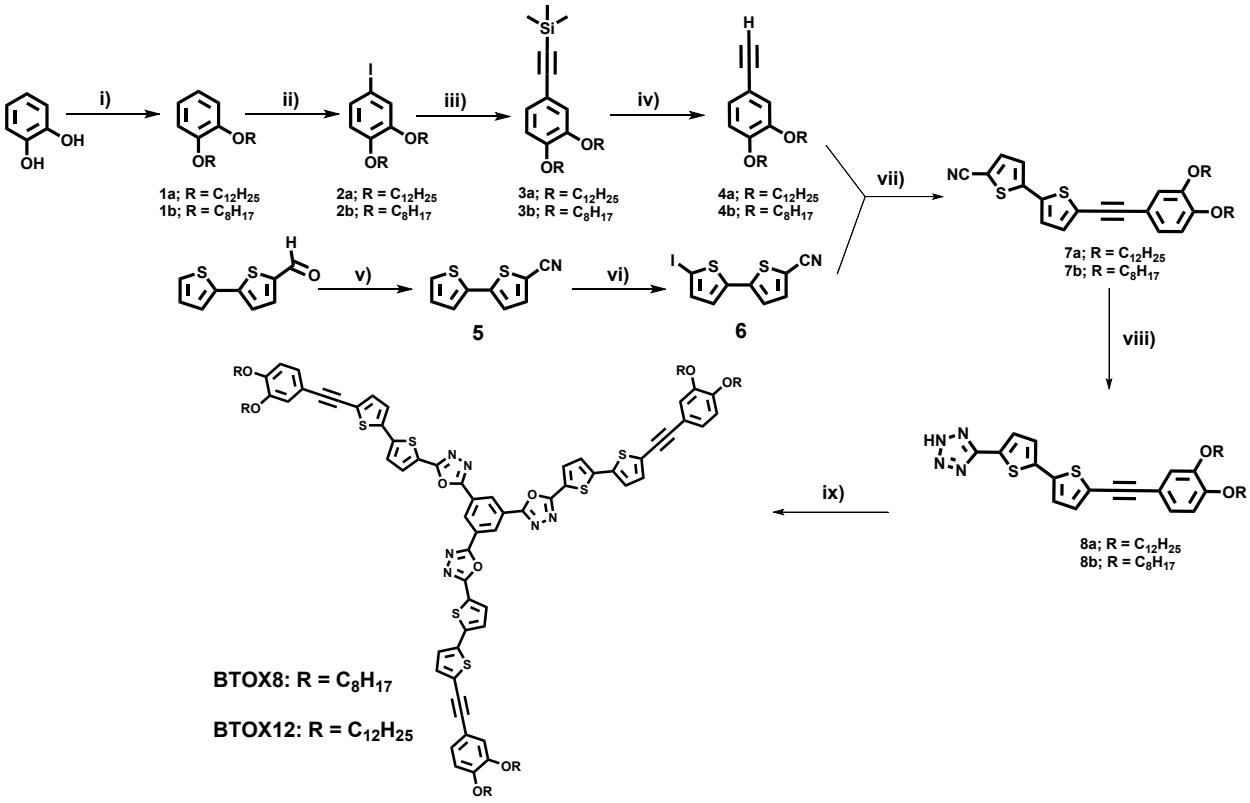
Contents

1. Experimental Section

1.1 Instrumentation. The solvents and the reagents were dried and purified by standard methods prior to use. ^{1}H (300 & 500 MHz) and ^{13}C NMR (125 MHz) spectral analysis were performed on a Brucker Avance DPX spectrometer with TMS as internal standard. FT-IR spectra were recorded on a Shimadzu IR Prestige-21 Fourier Transform Infrared Spectrophotometer. MALDI-TOF mass spectrometry was carried out on a Perspective Biosystems Voyager DE PRO MALDI-TOF mass spectrometer using α-cyano-4-hydroxy cinnamic acid as the matrix. Electronic absorption spectra were recorded on a Shimadzu UV-3101 PC NIR scanning spectrophotometer and emission spectra were recorded on a SPEX-Fluorolog FL-1039 spectrofluorimeter. Optical absorption measurements were carried out using 1 mm or 10 mm cuvettes. Fluorescence measurements were carried out using 1mm cuvette in a front face setup. Fluorescence quantum yields in solution were measured using 10-methylacridinium trifluoromethanesulfonate in water (ϕ_f = 0.99) as reference.[1] Fluorescence lifetimes were measured using IBH (FluoroCube) time-correlated picoseconds single photon counting (TCSPC) system. Samples were excited with a pulse diode laser (<100 ps pulse duration) at a wavelength of 401 nm for solution and 440 nm for self-assembled materials with a repetion rate of 1 MHz. The detection system consisted of a micro channel plate photomultiplier (5000U-09B, Hamamatsu) with a 38.6 ps response time coupled to a monochromator (5000m) and TCSPC electronics [Data station Hub including Hub-NL, nanoLED controller and preinstalled Fluorescence Measurement and Analysis Studio (FMAS) Software]. The fluorescence lifetime values were obtained using DAS6 decay analysis software. Atomic force microscopy (AFM) images were recorded under ambient conditions using NTEGRA Prima - NT-MDT, Russia, scanning probe microscope operated in tapping mode. Micro fabricated silicon cantilever tips (NSG 20) with a resonance frequency of 260–630 kHz and a force constant of 20–80 Nm^{-1} were used. The tip curvature radius was 10 nm. The scan rate was 1 Hz. The samples for AFM studies were prepared by drop casting the 2×10^{-4} M aggregated solution onto a freshly cleaved mica sheet and allowed to dry under ambient conditions. TEM measurements were carried out in JEOL 100 kV HRTEM. The samples were prepared by drop casting 25 μL of 2×10^{-4} M onto a carbon coated copper grid and solvent was allowed to evaporate under ambient condition. X-ray diffraction studies of xerogel was carried out on samples coated on an aluminium foil and measurements were recorded on a XEUSS SAXS / WAXS systems by XENOCS Cu Kα radiation (λ = 1.54 Å). The measurements were carried out in the transmission mode. Differential scanning calorimetry was performed using a Perkin-Elmer Pyris 6 DSC instrument in sealed aluminium pans under nitrogen flow, at a heat/cooling rate of 5 °C/min. DLS measurements were carried out in a ZETASIZER NANO-ZS device (Malvern Instruments Ltd., U. K.) at 298 K. Thermo gravimetric analysis (TGA) were performed on a TG/DTA-6200 instrument (SII Nano Technology Inc., Japan) in a nitrogen atmosphere.

2. Synthesis of BTOX derivatives



Scheme S1. Procedure for synthesis of **BTOX8** and **BTOX12**: i) R-Br, K_2CO_3, DMF, 80 °C, 24 h. ii) N-iodosuccinimide, Trifluoroacetic acid, CH_3CN, rt, 6 h. iii) Trimethylsilylacetylene, Pd(II)Cl_2, CuI, PPh_3, THF, Diisopropylamine, rt, 12 h. iv) TBAF, THF, rt, 4h. v) I_2, NH_3, THF, rt, 5h. vi) N-iodosuccinimide, glacial acetic acid, DCM, rt, 6 h. vii) Pd(II)Cl_2, CuI, PPh_3, THF, Diisopropylamine, rt, 12 h. viii) NaN_3, NH_4Cl, DMF, 100 °C, 12 h. ix) 1,3,5-Benzene tricarbonyl trichloride, pyridine, 120 °C, 12 h.

3. Characterization

3.1. General procedure for the synthesis of compound 1, 2-bis (alkoxy) benzene (1a and 1b):

Catechol (1 equiv), alkyl bromide (4 equiv) and K_2CO_3 (7 equiv) were dissolved in 30 mL of dry degassed DMF and were stirred at 80 °C for 24 h. The reaction mixture was then poured into ice cold water. The precipitate formed was filtered, washed with water and dried. The crude product was further purified by column chromatography using silica gel (100-200 mesh) as the stationary phase and hexane as the mobile phase.

1, 2- bis(dodecyloxy)benzene (1a): Yield 85%; colorless amorphous solid; ^{1}H NMR (300MHz, $CDCl_3$) δ 6.88 (s, 4H, aromatic), δ 3.96 - 4.00 (t, 4H, -OCH_2), δ 1.78 - 1.85 (m, 4H, -OCH_2CH_2), δ 1.26 - 1.47 (m, 36H, -CH_2), δ 0.85 – 0.90 (t, 6H,-CH_2CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 149.25, 121.0, 114.14, 69.29, 31.93, 29.72, 29.65, 29.45, 29.37, 26.06, 22.69, 14.12 ppm. IR (KBr) ν_{max}: 2951, 2914, 2850, 1587, 1508, 1461, 1455, 1390, 1257, 1220, 1122, 997, 732 cm^{-1}.

1, 2- bis(octyloxy)benzene (1a): Yield 81%; colorless liquid; ^{1}H NMR (300MHz, $CDCl_3$) δ 6.88 (s, 4H, aromatic), δ 3.96 - 4.00 (t, 4H, -OCH_2), δ 1.78 - 1.85 (m, 4H, -OCH_2CH_2), δ 1.26 - 1.47 (m, 20H, -CH_2), δ 0.85 – 0.90 (t, 6H,-CH_2CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 149.25, 121.0, 114.14, 69.29, 31.93, 29.72, 29.65, 29.45, 29.37, 26.06, 22.69, 14.12 ppm. IR (KBr) ν_{max}: 2951, 2914, 2850, 1587, 1508, 1461, 1455, 1390, 1257, 1220, 1122, 997, 732 cm^{-1}.

3.2. General procedure for the synthesis of compound 1,2-bis(alkoxy)-4-iodobenzene (2a and 2b):

1, 2-bis alkoxy benzene (1 equiv) and NIS (1.1 equiv) were dissolved in 20 mL of acetonitrile solvent. To this solution, 5 drops of trifluoroacetic acid was added and stirred for 6 h at room temperature. The reaction mixture was then extracted with dichloromethane solvent. The organic layer was washed thoroughly with sodium thiosulphate solution and dried over anhydrous sodium sulphate. The excess solvent was removed under reduced pressure and the crude product was further purified by column chromatography using silica gel (100-200 mesh) as the stationary phase and 5% EtOAc: hexane as the mobile phase.

1, 2-bis(dodecyloxy)-4-iodobenzene (2a): Yield 87%; colorless amorphous solid ^{1}H NMR (300MHz, $CDCl_3$): δ 7.16-7.19 (d, J = 8.4Hz, 1H, aromatic), δ 7.12 (s, 1H, aromatic), δ 6.60-6.628 (d, J = 8.4 Hz, 1H, aromatic), δ 3.924-3.967 (t, 4H,-OCH_2), δ 1.78-1.85 (m, 4H, -OCH_2CH_2), δ 1.26-1.47 (m, 36H,-CH_2), δ 0.85-0.90 (t, 6H,-CH_2CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 150.14, 149.78, 149.25, 129.80, 123.79, 122.68, 115.73, 95.96, 82.51, 69.43, 69.36, 31.94, 29.72, 29.62, 29.38, 29.18, 29.05, 25.98, 22.70, 14.12 ppm. IR (KBr) ν_{max}: 2950, 2922, 2841, 1590, 1508, 1461, 1391, 1254, 1131, 1070, 993, 840, 800, 721 cm^{-1}.

1,2-bis(octyloxy)-4-iodobenzene (2b): Yield 78%; colorless liquid ^{1}H NMR (300MHz, $CDCl_3$): δ 7.16-7.19 (d, J = 8.4Hz, 1H, aromatic), δ 7.12 (s, 1H, aromatic), δ 6.60-6.628 (d, J = 8.4 Hz, 1H, aromatic), δ 3.924-3.967 (t, 4H,-OCH_2), δ 1.78-1.85 (m, 4H, -OCH_2CH_2), δ 1.26-1.47 (m, 20H,-CH_2), δ 0.85-0.90 (t, 6H,-CH_2CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 150.14, 149.78, 149.25, 129.80, 123.79, 122.68, 115.73, 95.96, 82.51, 69.43, 69.36, 31.94, 29.72, 29.62, 29.38, 29.18, 29.05, 25.98, 22.70, 14.12 ppm. IR (KBr) ν_{max}: 2950, 2922, 2841, 1590, 1508, 1461, 1391, 1254, 1131, 1070, 993, 840, 800, 721 cm^{-1}.

3.3. General procedure for the synthesis of compound ((3, 4-bis(alkoxy)phenyl)ethynyl) trimethylsilane (3a and 3b):

To a 100 mL two necked round bottom flask kept under argon atmosphere, 30 mL of dry THF was taken. To this 1, 2-bis(alkoxy)-4-iodobenzene (1 equiv) was added and stirred for few seconds. To this a speck of palladium (II) chloride, CuI and PPh_3, was added followed by addition of 15 mL of dry diisopropylamine and stirred in an ice bath. To this trimethylsilylacetylene (2.5 equiv) was added drop wise using a syringe. The reaction mixture was stirred at room temperature for 12 h. It was then passed through a celite column. The crude product was then purified by column chromatography using silica gel (100-200 mesh) as the stationary phase and 5% EtOAc: hexane as the mobile phase.

((3, 4-bis(dodecyloxy)phenyl)ethynyl) trimethylsilane (3a): Yield 82%; colorless solid ^{1}H NMR (500MHz, $CDCl_3$): δ 6.944-6.927 (d, J = 8.5Hz, 1H, aromatic), δ 6.877 (s, 1H, aromatic), δ 6.665-6.648 (d, J = 8.5 Hz, 1H, aromatic), δ 3.885-3.858 (t, 4H,-OCH_2), δ 1.731-1.696 (m, 4H, -OCH_2CH_2), δ 1.263-1.159 (m, 36H,-CH_2), δ 0.888-0.773 (t, 6H,-CH_2CH_3), δ 0.15 (s, 9H, -CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 150.4, 146.3, 124.5, 114.9, 110.6, 110, 98.9, 69, 53.5, 31.9, 29.6, 29.3, 25.9, 22.7, 14.1, 3.4 ppm. IR (KBr) ν_{max}: 2950, 2922, 2841, 1590, 1508, 1461, 1391, 1254, 1131, 1070, 993, 840, 800, 721cm^{-1}.

((3, 4-bis(octyloxy)phenyl)ethynyl) trimethylsilane (3b): Yield 78%; colorless liquid ^{1}H NMR (500MHz, $CDCl_3$): δ 6.944-6.927 (d, J = 8.5Hz, 1H, aromatic), δ 6.877 (s, 1H, aromatic), δ 6.665-6.648 (d, J = 8.5 Hz, 1H, aromatic), δ 3.885-3.858 (t, 4H,-OCH_2), δ 1.731-1.696 (m, 4H, -OCH_2CH_2), δ 1.263-1.159 (m, 20H,-CH_2), δ 0.888-0.773 (t, 6H,-CH_2CH_3), δ 0.15 (s, 9H, -CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 150.4, 146.3, 124.5, 114.9, 110.6, 110, 98.9, 69, 53.5, 31.9, 29.6, 29.3, 25.9, 22.7, 14.1, 3.4 ppm. IR (KBr) ν_{max}: 2950, 2922, 2841, 1590, 1508, 1461, 1391, 1254, 1131, 1070, 993, 840, 800, 721cm^{-1}.

3.4. General procedure for the synthesis of compound 1, 2-bis(alkoxy)-4-ethynylbenzene (4a and 4b)

To a 100 mL two necked round bottom flask ((3, 4-bis(alkyloxy)phenyl)ethynyl) trimethylsilane (1 equiv) dissolved in 20 mL of dry THF was taken. To this tetra butyl ammonium fluoride (2 equiv) was added and stirred at room temperature for 4 h. The reaction mixture was then extracted with dichloromethane solvent. The organic layer was collected and dried over anhydrous sodium sulphate. The excess solvent was removed under reduced pressure. The crude product was further purified by column chromatography using silica gel (100-200 mesh) as the stationary phase and 5% EtOAc: Hexane as the eluent.

1, 2-bis(dodecyloxy)-4-ethynylbenzene (4a): Yield 96%; dark green colored solid ^{1}H NMR (500MHz, $CDCl_3$): δ 7.066-7.050 (d, J = 8 Hz, 1H, aromatic), δ 6.911 (s, 1H, aromatic), δ 6.796-6.780 (d, J = 8 Hz, 1H, aromatic), δ 4.002-3.958 (t, 4H,-OCH_2), δ 2.984(s, 1H, acetylenic) δ 1.468-1.53 (m, 4H, -OCH_2CH_2), δ 1.310-1.260 (m, 36H,-CH_2), δ 0.894-0.866 (t, 6H,-CH_2CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 150.4, 146.3, 124.5, 114.9, 110.6, 110, 82.3, 81.4, 69, 53.5, 31.9, 29.6, 29.3, 25.9, 22.7, 14.1 ppm. IR (KBr) ν_{max}: 3296, 2951, 2914, 2846, 2100, 1595, 1512, 1466, 1414, 1392, 1268, 1136, 1072, 999, 847, 806, 723, 667, 580 cm^{-1}.

1, 2-bis(octyloxy)-4-ethynylbenzene (4b): Yield 94%; dark colored liquid ^{1}H NMR (500MHz, $CDCl_3$): δ 7.066-7.050 (d, J = 8 Hz, 1H, aromatic), δ 6.911 (s, 1H, aromatic), δ 6.796-6.780 (d, J = 8 Hz, 1H,

aromatic), δ 4.002-3.958 (t, 4H,-OCH_2), δ 2.984(s, 1H, acetylenic) δ 1.468-1.53 (m, 4H, -OCH_2CH_2), δ 1.310-1.260 (m, 20H,-CH_2), δ 0.894-0.866 (t, 6H,-CH_2CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 150.4, 146.3, 124.5, 114.9, 110.6, 110, 82.3, 81.4, 69, 53.5, 31.9, 29.6, 29.3, 25.9, 22.7, 14.1 ppm. IR (KBr) ν_{max}: 3296, 2951, 2914, 2846, 2100, 1595, 1512, 1466, 1414, 1392, 1268, 1136, 1072, 999, 847, 806, 723, 667, 580 cm^{-1}.

3. 5. General procedure for the synthesis of compound 2, 2'-bithiophene-5-carbonitrile (5):

To a 100 mL round bottom flask 2, 2'-bithiophene-5-carbaldehyde (1 equiv) dissolved in 10 mL of THF was taken. To this 30 mL aq. NH_3 (25%) and I2 sublimed (1.1 equiv) was added and stirred at room temperature for 5 h. The reaction mixture was then extracted using dichloromethane solvent. The organic layer was washed thoroughly with water and sodium thiosulphate solution and dried over anhydrous sodium sulphate. The excess solvent was removed under reduced pressure and the crude product was further purified by column chromatography using silica gel (100-200 mesh) as the stationary phase and 5% EtOAc: hexane as the mobile phase.

Yield: 94%; grey colored solid 1H NMR (500MHz, $CDCl_3$): δ 7.459-7.451 (d, J = 4 Hz, 1H, aromatic), δ 7.459-7.451 (d, J = 5 Hz, 1H, aromatic), δ 7.221-7.215 (d, J = 3 Hz, 1H, aromatic), δ 7.067-7.059 (d, J = 4 Hz, 1H, aromatic), δ 7.009-6.991 (t, J = 4Hz, 1H, aromatic) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 147, 144, 137, 128, 124, 114 106 ppm. IR (KBr) ν_{max}: 3155, 3088, 2214, 1774, 1709, 1543, 1444, 1413, 1186, 1058, 788 cm^{-1}.

3. 6. General procedure for the synthesis of compound 5'-iodo-2, 2'-bithiophene-5-carbonitrile (6):

To a 100 mL round bottom flask 2, 2'-bithiophene-5-carbonitrile (1 equiv) dissolved in 20 mL of dichloromethane was taken. To this N-iodosuccinimide (1.1 equiv) and 10 mL of glacial acetic acid was added and stirred at room temperature for 6 h. The reaction mixture was then extracted using dichloromethane solvent. The organic layer was washed thoroughly with water and sodium thiosulphate solution and dried over anhydrous sodium sulphate. The excess solvent was removed under reduced pressure and the crude product was further purified by column chromatography using silica gel (100-200 mesh) as the stationary phase and 5% EtOAc: hexane as the mobile phase.

Yield 96%; green colored solid ^{1}H NMR (500MHz, $CDCl_3$): δ 7.519-7.511 (d, J = 4 Hz, 1H, aromatic), δ 7.219-7.211 (d, J = 4 Hz, 1H, aromatic), δ 7.080-7.072 (d, J = 4 Hz, 1H, aromatic), δ 6.953-6.945 (d, J = 4 Hz, 1H, aromatic) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 147, 144, 143.1, 138.2, 125.3, 124.8, 114.2, 109.6, 72.6 ppm. IR (KBr) ν_{max}: 3155, 3088, 2214, 1774, 1709, 1543, 1444, 1413, 1186, 1058, 873, 788 cm^{-1}.

3. 7. General procedure for the synthesis of compound 5'-((3, 4-bis(alkoxy)phenyl)ethynyl)-2, 2'-bithiophene-5-carbonitrile (7a and 7b):

To a 100 mL two necked round bottom flask kept under argon atmosphere, 30 mL of dry THF was taken. To this 5'-iodo-2, 2'-bithiophene-5-carbonitrile (1 equiv) was added. To this a speck of palladium (II) chloride, CuI and PPh_3, was added followed by addition of 15 mL of dry diisopropylamine and then 1, 2-bis(alkoxy)-4-ethynylbenzene (1.1 equiv) The reaction mixture was stirred at room temperature for an overnight. It was then passed through a celite column. The crude product was further purified by column chromatography using silica gel (100-200 mesh) as the stationary phase and 5% EtOAc: Hexane as the eluent.

5'-((3, 4-bis(dodecyloxy)phenyl)ethynyl)-2, 2'-bithiophene-5-carbonitrile (7a): Yield 92%; yellow colored solid ^{1}H NMR (500MHz, $CDCl_3$): δ 7.27 (s, 1H, aromatic), δ 7.18-7.16 (d, J =8 Hz, 1H, aromatic), δ 7.14-7.13 (d, J = 8 Hz, 1H, aromatic), δ 7.10-7.10 (d, J = 4 Hz, 1H, aromatic), δ 7.08-7.08 (d, J = 4 Hz, 1H, aromatic), δ 7.02-7.02 (d, J = 4 Hz, 1H, aromatic), δ 6.85-6.83 (d, J = 4 Hz, 1H, aromatic), δ 4.021-3.999 (t, 4H,-OCH_2), δ 1.835-1.806 (m, 4H, -OCH_2CH_2), δ 1.476-1.432 (m, 36H,-CH_2), δ 0.893-0.868 (t, 6H,-CH_2CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 150.4, 147, 146.3, 144, 138.4, 132.8, 124.8, 124.5, 123.5, 122.1, 114.9, 114.2, 110.6, 110, 109.6, 92.8, 86.9, 69, 29.6, 29.3, 25.9, 25.5, 22.7, 14.1 ppm. IR (KBr) ν_{max}: 2951, 2914, 2846, 2355, 2214, 1593, 1571, 1516, 1466, 1323, 1269, 1247, 1232, 1141, 997, 854, 794 cm^{-1}.

5'-((3, 4-bis(octyloxy)phenyl)ethynyl)-2, 2'-bithiophene-5-carbonitrile (7b): Yield 87%; yellow colored solid ^{1}H NMR (500MHz, $CDCl_3$): δ 7.27 (s, 1H, aromatic), δ 7.18-7.16 (d, J =8 Hz, 1H, aromatic), δ 7.14-7.13 (d, J = 8 Hz, 1H, aromatic), δ 7.10-7.10 (d, J = 4 Hz, 1H, aromatic), δ 7.08-7.08 (d, J = 4 Hz, 1H, aromatic), δ 7.02-7.02 (d, J = 4 Hz, 1H, aromatic), δ 6.85-6.83 (d, J = 4 Hz, 1H, aromatic), δ 4.021-3.999 (t, 4H,-OCH_2), δ 1.835-1.806 (m, 4H, -OCH_2CH_2), δ 1.476-1.432 (m, 20H,-CH_2), δ 0.893-0.868 (t, 6H,-CH_2CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 150.4, 147, 146.3, 144, 138.4, 132.8, 124.8, 124.5, 123.5, 122.1, 114.9, 114.2, 110.6, 110, 109.6, 92.8, 86.9, 69, 29.6, 29.3, 25.9, 25.5, 22.7, 14.1 ppm. IR (KBr) ν_{max}: 2951, 2914, 2846, 2355, 2214, 1593, 1571, 1516, 1466, 1323, 1269, 1247, 1232, 1141, 997, 854, 794 cm^{-1}.

3. 8. General procedure for the synthesis of compound 5-(5'-((3, 4-bis(alkoxy)phenyl)ethynyl)-2, 2'-bithiophen-5-yl)-2H-tetrazole (8a and 8b):

To a 250 mL two necked round bottom flask kept under argon atmosphere, 5'-((3, 4-bis(alkoxy)phenyl)ethynyl)-2, 2'-bithiophene-5-carbonitrile (1 equiv) dissolved in 30 mL dry degassed DMF solvent was taken. To this NaN_3 (2 equiv) and NH_4Cl (2 equiv) were added and stirred at 100 °C for 12 h. The reaction mixture was then poured into ice cold water. To this 100 mL of 20% HCl solution was added. The precipitate formed was then filtered, washed with water and dried. The crude product was then purified by column chromatography using silica gel (100-200 mesh) as the stationary phase and THF as the mobile phase.

5-(5'-((3, 4-bis(dodecyloxy)phenyl)ethynyl)-2, 2'-bithiophen-5-yl)-2H-tetrazole(8a): Yield 87%; Yellow colored amorphous solid ^{1}H NMR (500MHz, $CDCl_3$): δ 7.701 (s, 1H, aromatic), δ 7.228-7.221 (d, J = 3.5 Hz, 2H, aromatic), δ 7.167 (s, 1H, aromatic), δ 7.104-7.088 (d, J = 8 Hz, 1H, aromatic), δ 7.028 (s, 1H, aromatic), δ 6.848-6.831 (d, J = 8.5Hz, 1H, aromatic), δ 4.021-3.999 (t, 4H,-OCH_2), δ 1.835-1.806 (m, 4H, -OCH_2CH_2), δ 1.476-1.432 (m, 36H,-CH_2), δ 0.893-0.868 (t, 6H,-CH_2CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 163.5, 150.4, 146.3, 143.5, 138.4, 136.6, 132.8, 128.4, 124.5, 123.5, 122.1, 114.9, 110.6, 92.8, 86.9, 69, 29.6, 29.3, 25.9, 25.5, 22.7, 14.1 ppm. IR (KBr) ν_{max}: 2914, 2846, 1593, 1516, 1466, 1248, 1140, 1055, 958, 789 cm^{-1}.

5-(5'-((3, 4-bis(octyloxy)phenyl)ethynyl)-2, 2'-bithiophen-5-yl)-2H-tetrazole (8b):

Yield 80%; Yellow colored amorphous solid ^{1}H NMR (500MHz, $CDCl_3$): δ 7.701 (s, 1H, aromatic), δ 7.228-7.221 (d, J = 3.5 Hz, 2H, aromatic), δ 7.167 (s, 1H, aromatic), δ 7.104-7.088 (d, J = 8 Hz, 1H, aromatic), δ 7.028 (s, 1H, aromatic), δ 6.848-6.831 (d, J = 8.5Hz, 1H, aromatic), δ 4.021-3.999 (t, 4H,-OCH_2), δ 1.835-1.806 (m, 4H, -OCH_2CH_2), δ 1.476-1.432 (m, 20H,-CH_2), δ 0.893-0.868 (t, 6H,-CH_2CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 163.5, 150.4, 146.3, 143.5, 138.4, 136.6, 132.8, 128.4, 124.5, 123.5,

122.1, 114.9, 110.6, 92.8, 86.9, 69, 29.6, 29.3, 25.9, 25.5, 22.7, 14.1 ppm. IR (KBr) ν_{max}: 2914, 2846, 1593, 1516, 1466, 1248, 1140, 1055, 958, 789 cm^{-1}.

3. 9. General procedure for the synthesis of compound 1, 3, 5-tris(5-(5'-((3, 4-bis(alkoxy)phenyl) ethynyl)-2, 2'-bithiophen-5-yl)-1, 3, 4-oxadiazol-2-yl)benzene (**BTOX12** and **BTOX8**):

To a 250 mL two necked round bottom flask kept under argon atmosphere, acid chloride (1equiv) dissolved in 10 mL of dry degassed pyridine was taken. To this 5-(5'-((3,4-bis (alkoxy)phenyl)ethynyl)-2,2'-bithiophen-5-yl)-2H-tetrazole (3.6 equiv) dissolved in 30 mL of dry degassed pyridine was added drop wise using a pressure equalizer with constant stirring at room temperature for 15 min. The reaction mixture was then heated at 120 °C for 12 h. The reaction mixture was then poured into ice cold water. The precipitate formed was then filtered, washed with water and dried. The crude product was then purified by column chromatography by using silica gel (100-200 mesh) as the stationary phase and 30% EtOAc: hexane as the mobile phase.

1, 3, 5-tris(5-(5'-((3, 4-bis(dodecyloxy)phenyl)ethynyl)-2, 2'-bithiophen-5-yl)-1, 3, 4-oxadiazol-2-yl)benzene (**BTOX12**): Yield 62%; brown colored amorphous solid ^{1}H NMR (500MHz, $CDCl_3$): δ 8.974 (s, 3H, aromatic), δ 7.701 (s, 3H, aromatic), δ 7.228-7.221 (d, J = 3.5 Hz, 6H, aromatic), δ 7.167 (s, 3H, aromatic), δ 7.104-7.088 (d, J = 8 Hz, 3H, aromatic), δ 7.028 (s, 3H, aromatic), δ 6.848-6.831 (d, J = 8.5Hz, 3H, aromatic), δ 4.021-3.999 (t, 12H, -OCH_2), δ 1.835-1.806 (m, 12H, -OCH_2CH_2), δ 1.476-1.432 (m, 108H, -CH_2), δ 0.893-0.868 (t, 18H,-CH_2CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 161.9, 161.2, 150.4, 146.3, 138.4, 136.6, 132.8, 131.8, 128.4, 127.1, 125.4, 124.5, 123.5, 114.9, 110.6, 110, 92.8, 86.9, 69, 31.9, 29.6, 29.3, 25.9, 25.5, 22.7, 14.1 ppm. IR (KBr) ν_{max}: 2918, 2849, 1726, 1583, 1512, 1491, 1466, 1319, 1252, 1225, 1209, 1138, 798, 723, 675 cm^{-1}. MS (MALDI-TOF) calculated for $C_{132}H_{174}N_6O_9S_6$ ($M+H^+$) (2182.23); found 2183.05

1, 3, 5-tris(5-(5'-((3, 4-bis(octyloxy)phenyl)ethynyl)-2, 2'-bithiophen-5-yl)-1, 3, 4-oxadiazol-2-yl)benzene (**BTOX8**): Yield 57%; brown colored amorphous solid ^{1}H NMR (500MHz, $CDCl_3$): δ 8.974 (s, 3H, aromatic), δ 7.701 (s, 3H, aromatic), δ 7.228-7.221 (d, J = 3.5 Hz, 6H, aromatic), δ 7.167 (s, 3H, aromatic), δ 7.104-7.088 (d, J = 8 Hz, 3H, aromatic), δ 7.028 (s, 3H, aromatic), δ 6.848-6.831 (d, J = 8.5Hz, 3H, aromatic), δ 4.021-3.999 (t, 12H, -OCH_2), δ 1.835-1.806 (m, 12H, -OCH_2CH_2), δ 1.476-1.432 (m, 60H, -CH_2), δ 0.893-0.868 (t, 18H,-CH_2CH_3)ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 161.9, 161.2, 150.4, 146.3, 138.4, 136.6, 132.8, 131.8, 128.4, 127.1, 125.4, 124.5, 123.5, 114.9, 110.6, 110, 92.8, 86.9, 69, 31.9, 29.6, 29.3, 25.9, 25.5, 22.7, 14.1 ppm. IR (KBr) ν_{max}: 2918, 2849, 1726, 1583, 1512, 1491, 1466, 1319, 1252, 1225, 1209, 1138, 798, 723, 675 cm^{-1}. MS (MALDI-TOF) calculated for $C_{108}H_{126}N_6O_9S_6$ ($M+H^+$) (1845.59); found 1846.22

4. Additional Figures

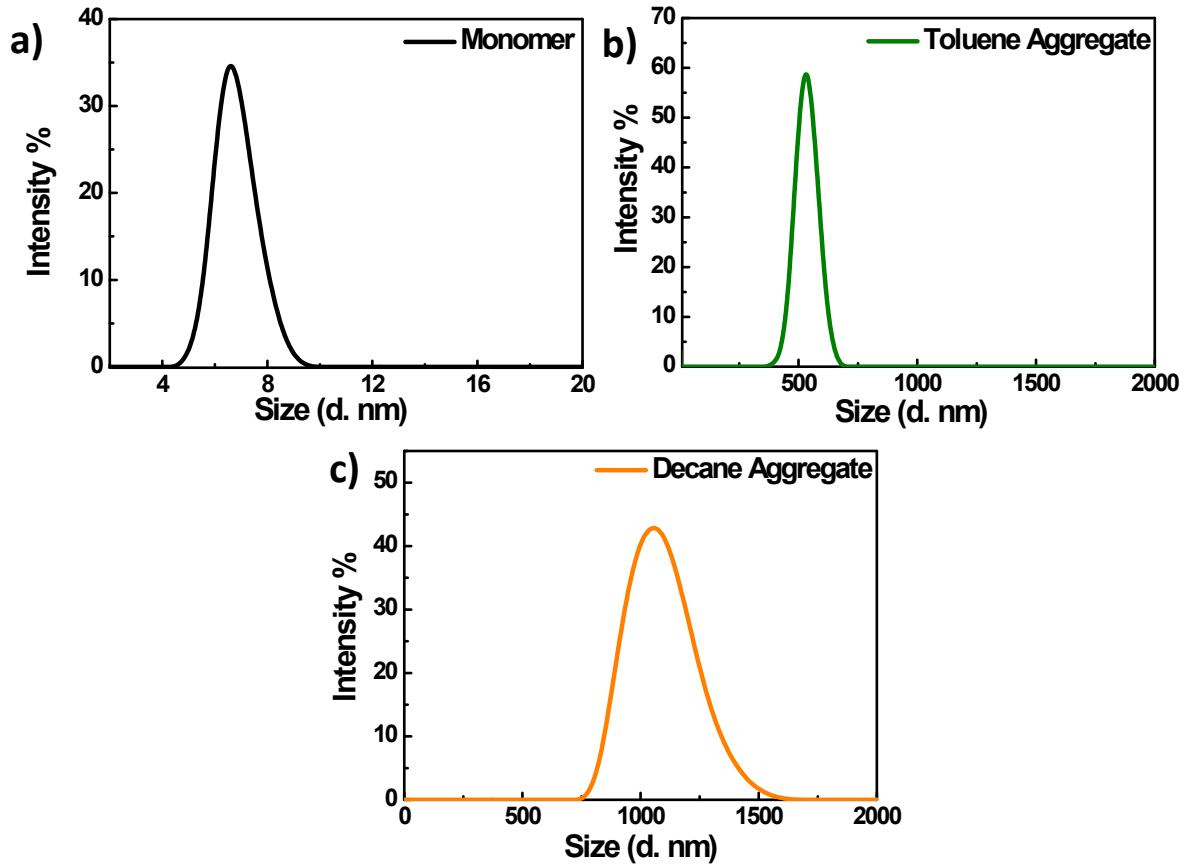


Figure S1. Dynamic light scattering spectra of **BTOX12** in a) 1×10^{-7} M in toluene b) 2×10^{-4} M solution in toluene and c) 2×10^{-4} M solution in *n*-decane

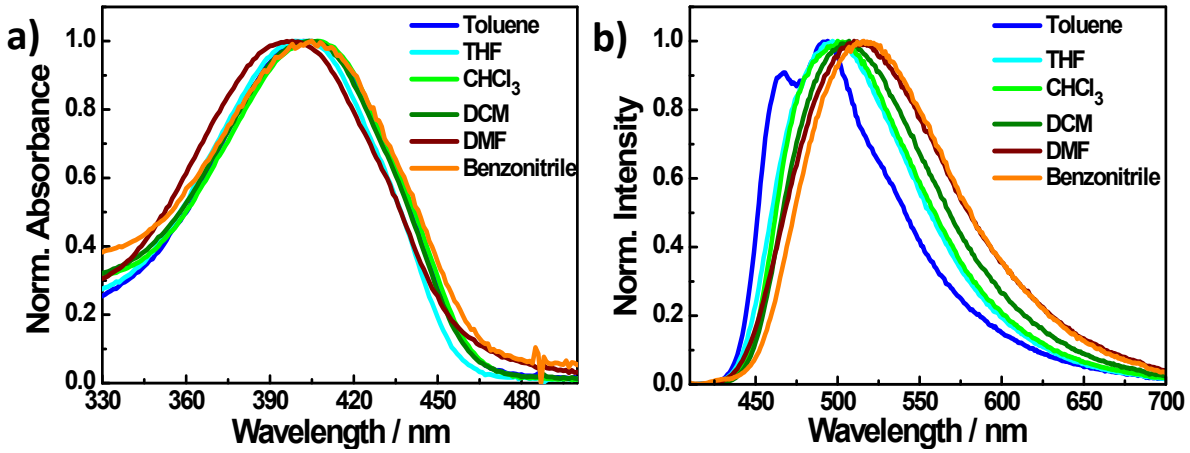


Figure S2. a) Absorption and b) emission spectra (λ_{ex} = 400 nm) of **BTOX12** in different solvents

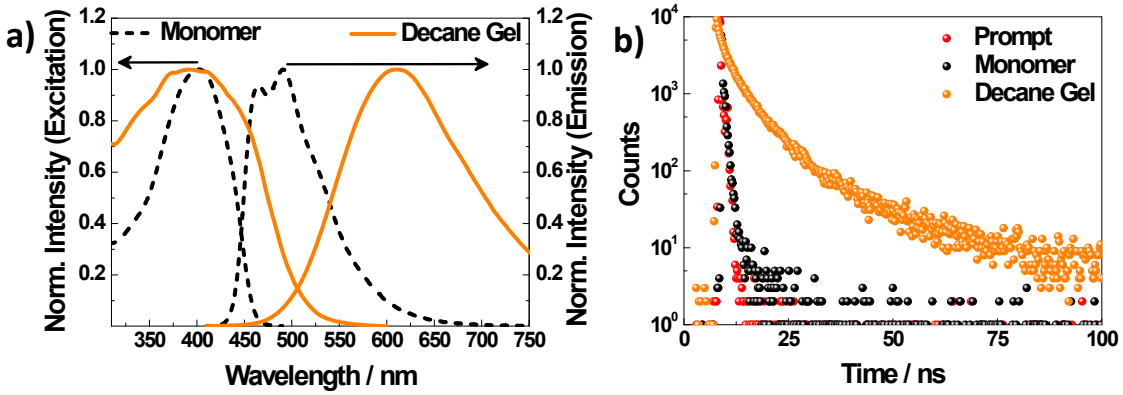


Figure S3. a) Excitation (λ_{em} monitored at emission maximum) and emission spectra (λ_{ex} = 400 nm) and b) Fluorescence lifetime decay profile (λ_{em} monitored at emission maximum) of **BTOX12** in gel state and under dilute conditions in *n*-decane

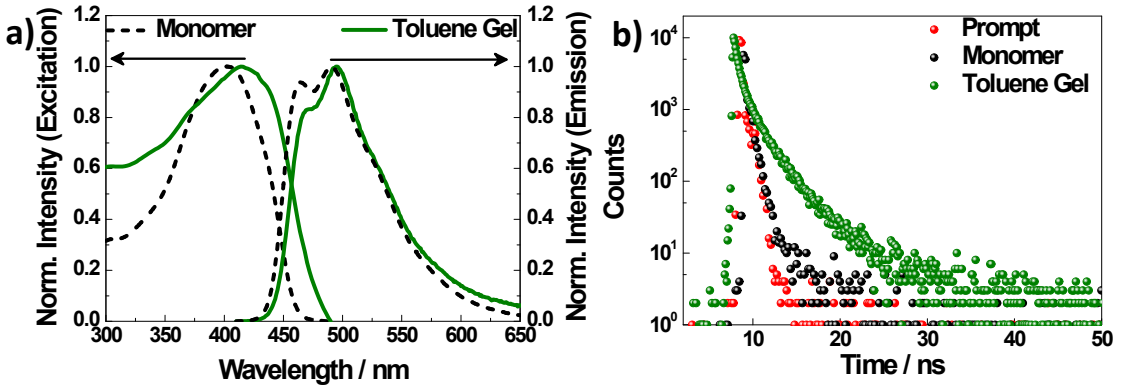


Figure S4. a) Excitation (λ_{em} monitored at emission maximum) and emission spectra (λ_{ex} = 400 nm) and b) Fluorescence lifetime decay profile (λ_{em} monitored at emission maximum) of **BTOX12** in gel state and under dilute conditions in toluene

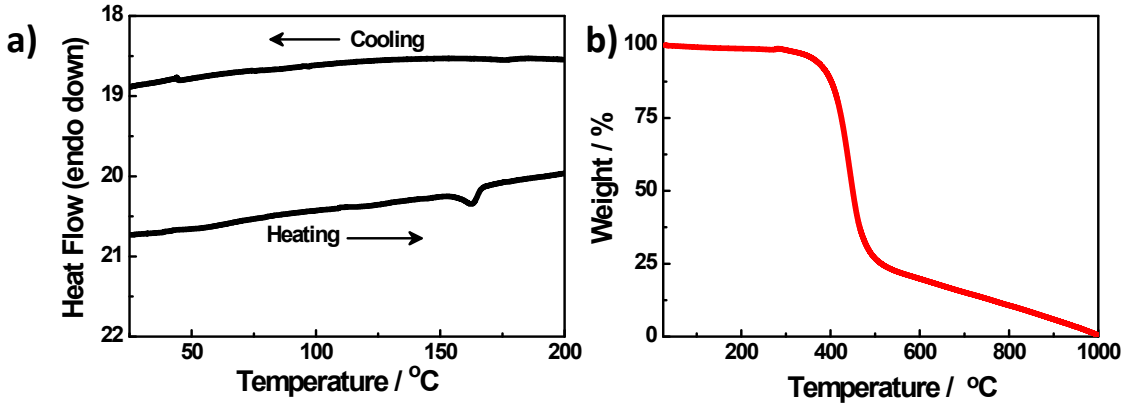


Figure S5. a) DSC and b) TG analysis of **BTOX12** derivative

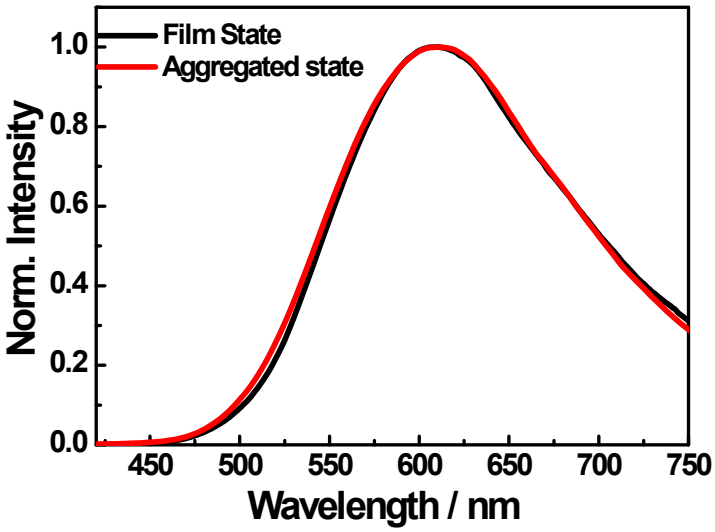


Figure S6. Normalised emission spectra (λ_{ex} = 400 nm) of **BTOX12** in aggregated state (red line) and in film state (black line)

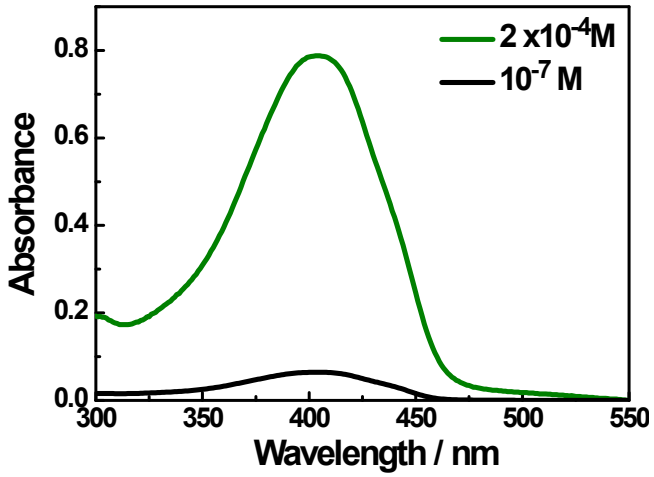


Figure S7. Absorption spectra of 10^{-7}M (black line) and 2×10^{-4}M (green line) of BTOX12 in toluene

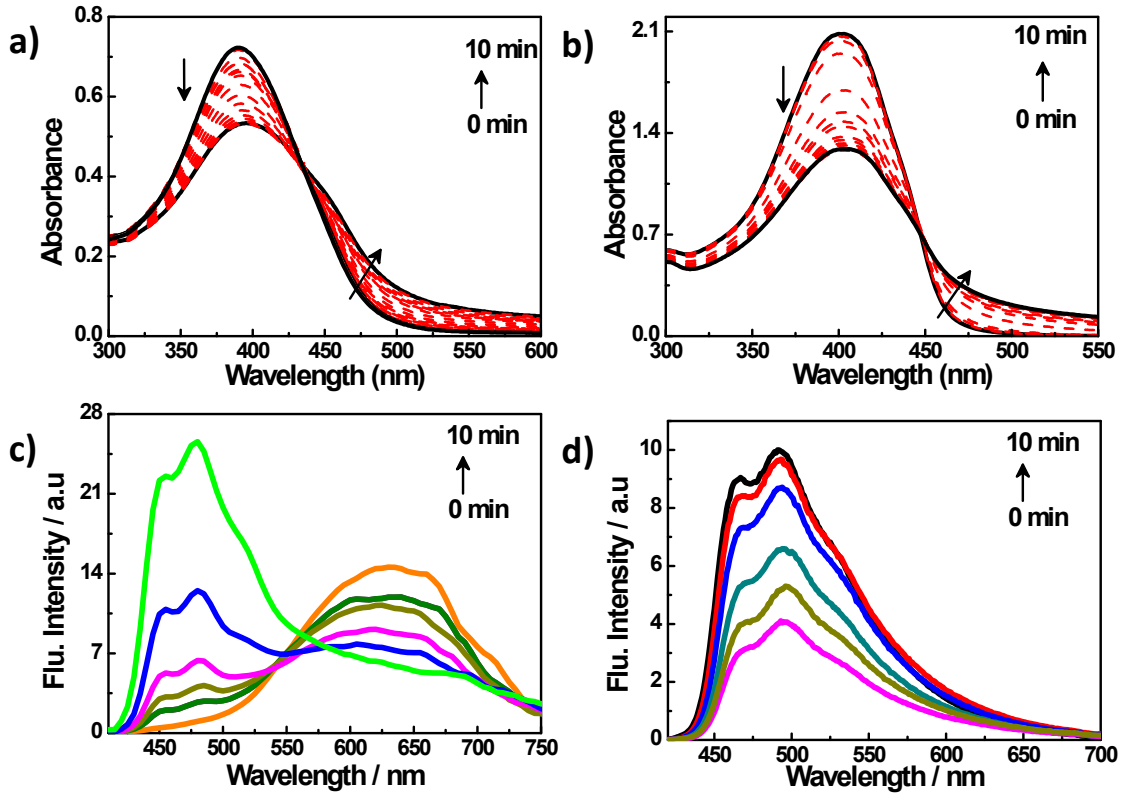


Figure S8. Time dependent changes in absorption spectra of BTOX12 in a) n-decane and b) toluene. Time dependent changes in emission spectrum of BTOX12 in c) n-decane and d) toluene

Table S1. Absorption, Emission, Fluorescence quantum yield and Fluorescence lifetime values of **BTOX12** in different solvents.

Solvent	Abs. λ_{abs} (nm)	Em. λ_{em} (nm)	Φ_f	τ_f (ns)	χ^2
Toluene	399	466, 493	0.22	0.25	1.06
THF	400	500	0.31	0.37	1.14
Chloroform	403	500	0.35	0.45	1.01
DCM	403	507	0.36	0.51	1.19
DMF	398	510	0.39	0.75	1.04
Benzonitrile	405	516	0.31	1.13	1.01

Table S2. Fluorescence lifetime decay values of **BTOX12** in gel state in toluene and *n*-decane

Sample	λ_{max} (nm)	τ_F	χ^2
Toluene	500	T_1= 0.38 ns (78.85%) T_2= 1.42 ns (16.10%) T_3= 3.32 ns (5.05%)	1.16
n-Decane	610	T_1= 1.19 ns (17.75%) T_2= 4.79 ns (61.38%) T_3= 15.75 ns (20.87%)	1.09

5. Reference

1. S. A. Jonker, F. Ariese, J. W. Verhoeven, *Recl. Trav. Chim. Pays Bas* **1989**, *108*, 109-114; G. Weber, F. W. J. Teale, *Trans. Faraday Soc*. **1957**, *53*, 646.