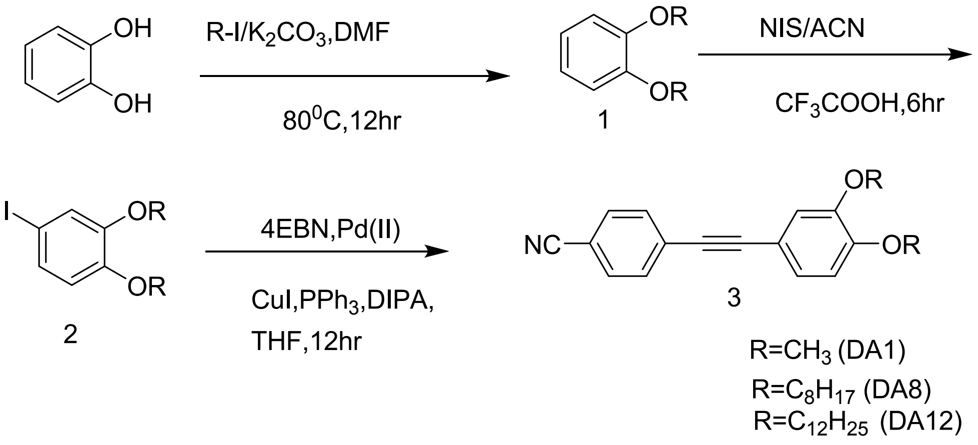
Transformation of Photophysical Properties From Solution to Solid State in Alkoxy-Cyano-Diphenylacetylene Molecules

Venugopal Karunakaran[a,b]***, *Deepak D. Prabhu*[a], *Suresh Das*[a,c]***, *Sunil Varughese*[d]

[a]Photosciences and Photonics Section, Chemical Sciences and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology, Thiruvananthapuram 695 019, Kerala, India. [b]Academy of Scientific and Innovative Research (AcSIR), New Delhi 110 001, India. [c]Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560 064, India, [d]Materials Sciences and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology, Thiruvananthapuram 695 019, Kerala

1 Synthesis of dialkoxy derivatives



Scheme 1 Synthesis of 4-[(3,4-bisalkoxyphenyl)ethynyl]benzonitrile

NIS: N-Iodosuccinimde, 4EBN: Ethynyl benzonitrile, DIPA: diisopropylamine

1.1 Synthesis of 1, 2-bis (alkoxy) benzene (1)

Catechol (1 equiv) and K_2CO_3 (7 equiv) were dissolved in 30 mL of acetonitrile and were stirred in ice bath. To this alkyl iodide (4 equiv.) was added dropwise with constant stirring. Then the reaction temperature was increased to 80°c and stirred at that temperature for another 12 hr. The reaction mixture was then poured in to ice cold water and extracted using chloroform. The organic layer was washed thoroughly with water and dried over anhydrous sodium sulphate. The crude product obtained was further purified by column chromatography using silicagel (100-200mesh) as the stationary phase and hexane as the mobile phase.

1, 2-bis(methoxy) benzene(1a)

Yield: 85%; Colorless amorphous solid.

1H NMR (300 MHz, CDCl3) δ 6.88 (s, 4H), 3.92 (s, 6H) ppm. ^{13}C NMR (125 MHz, CDCl3): 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(1b)

Yield: 81%; colourless amorphous solid.

1H NMR (300MHz, CDCl3) δ 6.88 (s, 4H, aromatic), 3.96-4.00 (t, 4H, -OCH2), 1.78-1.85 (m, 4H, -OCH2CH2), 1.26-1.47 (m, 20H, -CH2), 0.85-0.90 (t, 6H,-CH2CH3) ppm. ^{13}C NMR (125 MHz, CDCl3): 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(dodecyloxy)benzene(1c)

85%; Colorless amorphous solid

^1H NMR (300 MHz, $CDCl_3$) δ 6.88 (s, 4H), 3.96-4.00 (t, 4H), 1.78-1.85 (m, 4H), 1.26-1.47 (m, 36H), 0.85-0.90 (t, 6H) 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 Synthesis of 1,2-bis(alkoxy)-4-iodobenzene (2)

1, 2-bis (alkoxy) benzene (1 equiv.) and N - Iodosuccinimide (1.1 equiv) were dissolved in 20 ml of acetonitrile solvent to which, 5 drops of tri fluoro acetic acid was added and stirred for 6 hr at room temperature. The reaction mixture was then extracted with dichloromethane solvent and the organic layer was washed thoroughly with sodium thiosulphate solution, 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 (100-200mesh) as the stationary phase and 5%EtOAc: Hexane as the mobile phase.

1, 2- bis(methoxy)-4-iodobenzene(2a)

Yield: 87%; colorless amorphous solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.16-7.19 (d, J = 8.4 Hz, 1H), 7.12 (s, 1H), 6.60-6.62 (d, J = 8.4 Hz, 1H), 3.92 (s, 4H) 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}.

1, 2- bis(dodecyloxy)-4-iodobenzene(2c)

Yield: 87%; colorless amorphous solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.16-7.19 (d, *J* = 8.4 Hz, 1H), 7.12 (s, 1H), 6.60-6.62 (d, *J* = 8.4 Hz, 1H), 3.92-3.96 (t, 4H), 1.78-1.85 (m, 4H), 1.26-1.47 (m, 36H), 0.85-0.90 (t, 6H) 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}.

1.3 Synthesis of 4-((3, 4-bis (alkoxy) phenyl) ethynyl) benzonitrile (3):

To a 100 ml two necked round bottom flask kept under argon atmosphere ,1,2-bis(alkoxy)-4-iodobenzene (1.1 equiv.),4-ethynylbenzonitrile (1 equiv.) and a catalytic amounts of palladium (II) chloride, CuI and PPh_3 were added to 15ml of degassed THF. To this 10 ml of degassed diisopropyl amine was added and stirred at room temperature for 12hr. The reaction mixture was then passed through a celite column and the crude product was further purified by column chromatography using silica gel (100-200 mesh)as the stationary phase and 5% EtOAc: Hexane a s the mobile phase.Yield:82%

DA1:

^{1}H NMR ($CDCl_3$, 500 MHz):δ = 7.622 – 7.638 (d, *J = 8Hz*, 2H), 7.578 – 7.595 (d, *J = 8.5Hz*, 2H), 7.155 – 7.172 (d, *J = 8.5Hz*, 1H), 7.040 (s, 1H), 6.856 – 6.873 (d, J = 8.5, 1H), 3.920 (s, 6H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 150.21, 148.77, 132.04, 131.87, 128.50, 125.38, 118.60, 114.30, 111.12, 111.09, 94.17, 86.57, 77.28, 77.03, 76.78, 55.97, 55.95 ppm. HRMS (ESI+): $[M+H]^+$ calcd for $C_{17}H_{13}NO_2$: m/z =264.1019, (found, m/z = 264.101). IR (KBr), $\bar{\nu}$ = 2,837 (SP^3 C–H stretch), 2,957 (SP^2 C–H stretch), 2,226 (C ≡ C stretch), 2,206 (C ≡ N stretch), 1,517 (Aromatic C = C stretch), 1,254 and1,021 (C–O stretch) cm^{-1}.

DA8:

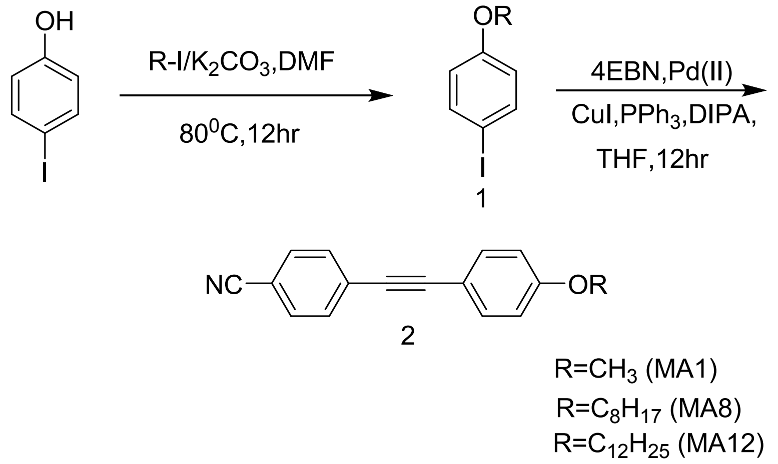
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.612 – 7.628 (d, *J = 8Hz*, 2H), 7.583 – 7.566 (d, *J = 8.5Hz*, 2H), 7.105 – 7.122(d, *J= 8.5Hz*,1H) ,7.036 (S, 1H) , 6.835 – 6.852(d, *J = 8.5 Hz*, 1H), 4.032, 3.997 (m, 4H), 1.860, 1.804(m, 4H), 1.488, 1.444 (m, 4H), 1.360, 1.289(m , 16H) .900 , .874 (m,6H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ 150.45, 132.02, 131.84, 125.39, 116.67, 113.11, 69.33, 69.12, 31.81, 29.35, 29.26, 29.14, 25.99, 22.66, 14.09 ppm. . HRMS (ESI+): $[M+H]^+$ calcd for $C_{31}H_{41}NO_2$: m/z = 460.321, (found m/z = 460.321). IR (KBr) $\bar{\nu}$ = 2,915

(SP^3 C–H stretch), 2,954 (SP^2 C–H stretch), 2,227 (C ≡ C stretch), 2,198 (C ≡ N stretch), 1,518 (Aromatic C = C stretch), 1,228 and 1,118 (C–O stretch) cm^{-1}.

DA12:

^1H NMR($CDCl_3$, 500 MHz):δ = 7.612 – 7.628 (d, *J = 8Hz*, 2H), 7.566 – 7.582(d, *J = 8 Hz*, 2H) , 7.104 -7.120 (d, *J = 8Hz*,2H), 7.036 (s, 1H), 6.835 – 6.851(d, *J = 8Hz*, 1H), 4.032, 3.995 (m, 4H), 1.858, 1.802 (m, 4H), 1.484, 1.443(m, 4H), 1.357, 1.263(m, 31H), 0.894, 0.867 (m, 7H) ppm. ^{13}C NMR ($CDCl_3$, 125MHz):δ = 150.82, 148.66, 132.01, 131.84, 125.0, 116.68, 114.10, 113.12, 69.33, 69.12, 31.93, 29.70, 29.66, 29.63, 29.40, 29.37, 29.20, 29.15, 26.01, 22.69, 14.11 ppm. HRMS (ESI+): $[M+H]^+$ calcd for $C_{39}H_{57}NO_2$: m/z = 572.446, (found, m/z =571.438). IR (KBr) $\bar{\nu}$ = 2,914 (SP^3 C–H stretch), 2,953 (SP^2 C–H stretch), 2,226 (C ≡ C stretch), 2,196 (C ≡ N stretch), 1,469 (Aromatic C = C stretch), 1,259 and 1,118 (C–O stretch) cm^{-1}.

2 Synthesis of monoalkoxy derivatives



Scheme 2 Synthesis of 4-[(4-alkoxyphenyl)ethynyl]benzonitrile

NIS: N-Iodosuccinimde, 4EBN: Ethynyl benzonitrile, DIPA: diisopropylamine

2.1 Synthesis of Alkoxy iodo benzene (1)

Iodo Phenol (1 equiv) and K_2CO_3 (7 equiv) were dissolved in 30 mL of DMF and were stirred in ice bath. To this alkyl iodide (4 equiv.) was added dropwise with constant stirring. Then the reaction temperature was increased to 80°c and stirred at that temperature for another 12 hr. The reaction mixture was then poured in to ice cold water and extracted using chloroform. The organic layer was washed thoroughly with water and dried over anhydrous sodium sulphate. The crude product obtained was further purified by column chromatography using silica gel (100-200mesh) as the stationary phase and hexane as the mobile phase. Yield: 85%; colourless amorphous solid.

2.2 Synthesis of 4-((4- alkoxy phenyl) ethynyl) benzonitrile (2)

To a 100 ml two necked round bottom flask kept under argon atmosphere, alkoxy-4-iodobenzene (1.1 equiv.),4 ethynyl benzonitrile(1 equiv.) and a catalytic amounts of palladium (II) chloride, CuI and PPh_3 were added to 15ml of degassed THF. To this 10 ml of degassed diisopropyl amine was added and stirred at room temperature for 12 hr. The reaction mixture was then passed through a celite column 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:82%

MA1: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.613 – 7.629(d, *J =8Hz*, 2H), 7.566 – 7.583 (d, *J = 8.5Hz*, 2H), 7.476 – 7.493(d, *J = 8.5Hz,* 2H), 6.893 - 6.910 (d, *J =8.5Hz,* 2H), 3.844 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 125MHz): δ = 160.28, 133.36, 132.02, 131.85, 128.65, 118.64, 114.25, 111.01, 94.10, 86.72, 55.36, 30.92 ppm. HRMS (ESI+): $[M+H]^+$ calcd for $C_{16}H_{11}NO$: m/z = 234.09134 (found m/z = 234.09097). IR (KBr), $\bar{\nu}$ = 2,847 (SP^3 C–H stretch), 2,971 (SP^2 C–H stretch) , 2,227 (C ≡ C stretch), 2,211 (C ≡ N stretch), 1,511 (Aromatic C=C stretch), 1,254, 1,027 (C–O stretch) cm^{-1}.

MA8: ^1H NMR ($CDCl_3$, 500MHz): δ = 7.611 – 7.627 (d, *J= 8Hz*, 2H), 7.561 – 7.578(d, *J = 8.5Hz*, 2H), 7.457 – 7.474(d, *J = 8.5Hz*, 2H), 6.875 – 6.892(d, *J =8.5Hz*,2H), 3.991, 3.965(t, 2H), 1.820, 1.764(m, 2H), 1.486, 1.428(m, 2H), 1.380,1.291(m, 2H), .904, .876 (m,2H)ppm ^{13}C NMR ($CDCl_3$, 125MHz): δ = 159.91, 133.33, 132.01, 131.83, 128.71, 114.68, 113.94, 110.96, 94.26, 68.16, 31.80, 30.93, 29.33, 29.22, 29.15, 26.00, 22.65, 14.09 ppm. HRMS (ESI+): $[M+H]^+$ calcd for $C_{23}H_{25}NO$: m/z = 332.201, (found m/z = 332.201). IR (KBr), $\bar{\nu}$ = 2,850 (SP^3 C–H stretch), 2,916 (SP^2 C–H stretch), 2,235(C≡C stretch), 2,211 (C ≡ N stretch), 1,514 (Aromatic C=C stretch), 1,243 and 1181(C–O stretch) cm^{-1}.

MA12: : ^1H NMR ($CDCl_3$, 500 MHz): δ =7.613 – 7.609 (d, J = 8.5Hz,2H), 7.561 – 7.578 (d, 8.5Hz,2H), 7.456 – 7.473(d, J = 8.5Hz, 2H), 6.875-6.892(d, J = 8.5Hz,2H) , 3.991, 3.965 (t, 2H), 1.819,1.762(m, 2H), 1.469, 1.425 (m,2H), 1.351, 1.266, (m, 8H), 0.895, 0.868 (m, 3H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 133.33, 132.01, 131.83, 114.68, 94.26, 86.64, 68.16, 31.91, 30.92, 29.65, 29.63, 29.55, 29.36, 29.34, 29.14, 25.99, 22.68, 14.11 ppm. HRMS_(ESI+): $[M+H]^+$ calcd for $C_{27}H_{33}NO$: m/z = 388.263, (found m/z = 388.263). IR (KBr), $\bar{\nu}$ = 2,848 (SP^3 C–H stretch), 2,918 (SP^2 C–H stretch), 2,236 (C ≡ C stretch), 2,211 (C ≡ N stretch), 1,513 (Aromatic C=C stretch), 1,243 and 1,180 (C–O stretch) cm^{-1}.

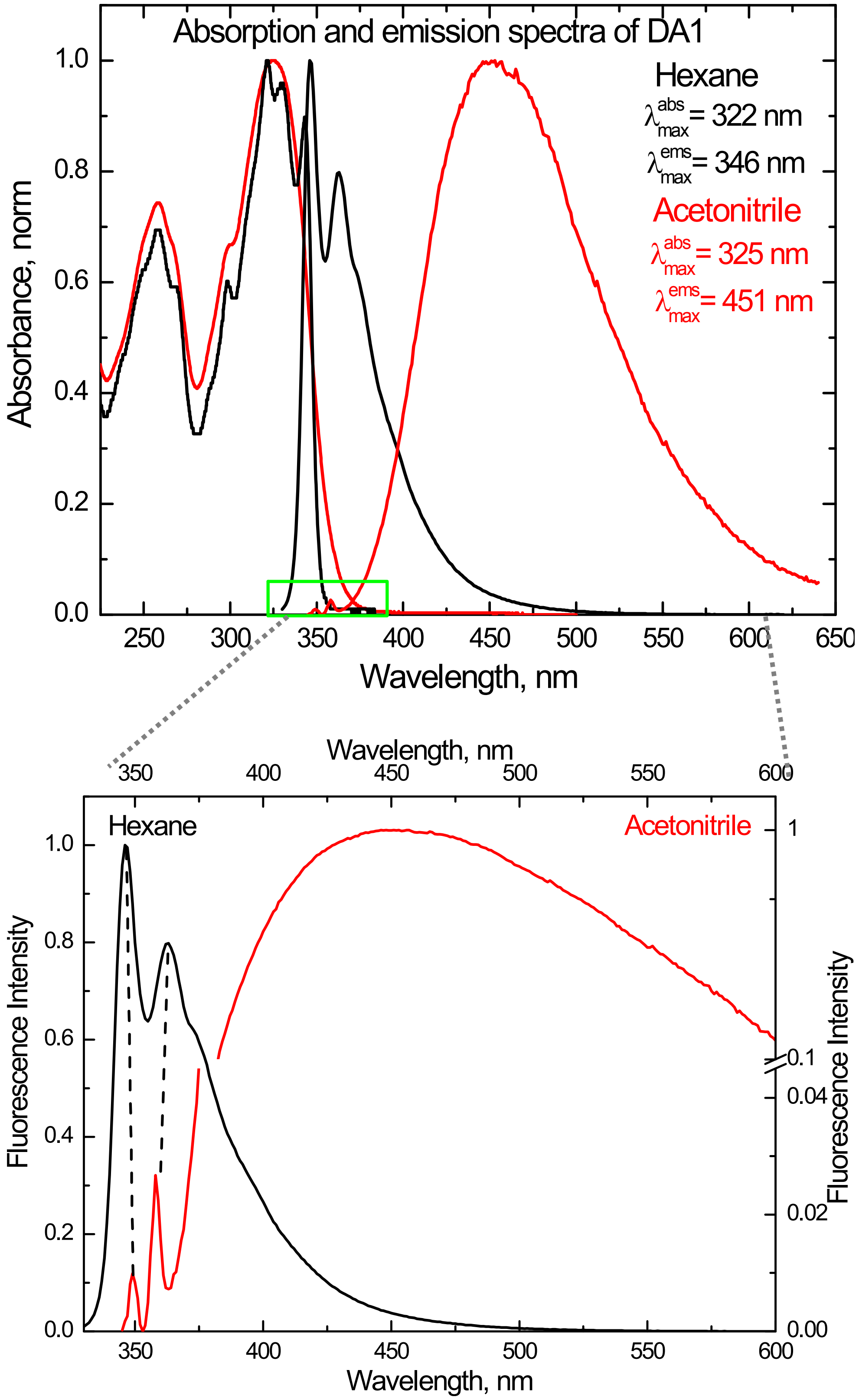


Figure S1 (a) Absorption, emission and excitation spectra of **DA1** in acetonitrile and cyclohexane. (b) Enlarged emission spectra of DA1 in acetonitrile and cyclohexane.

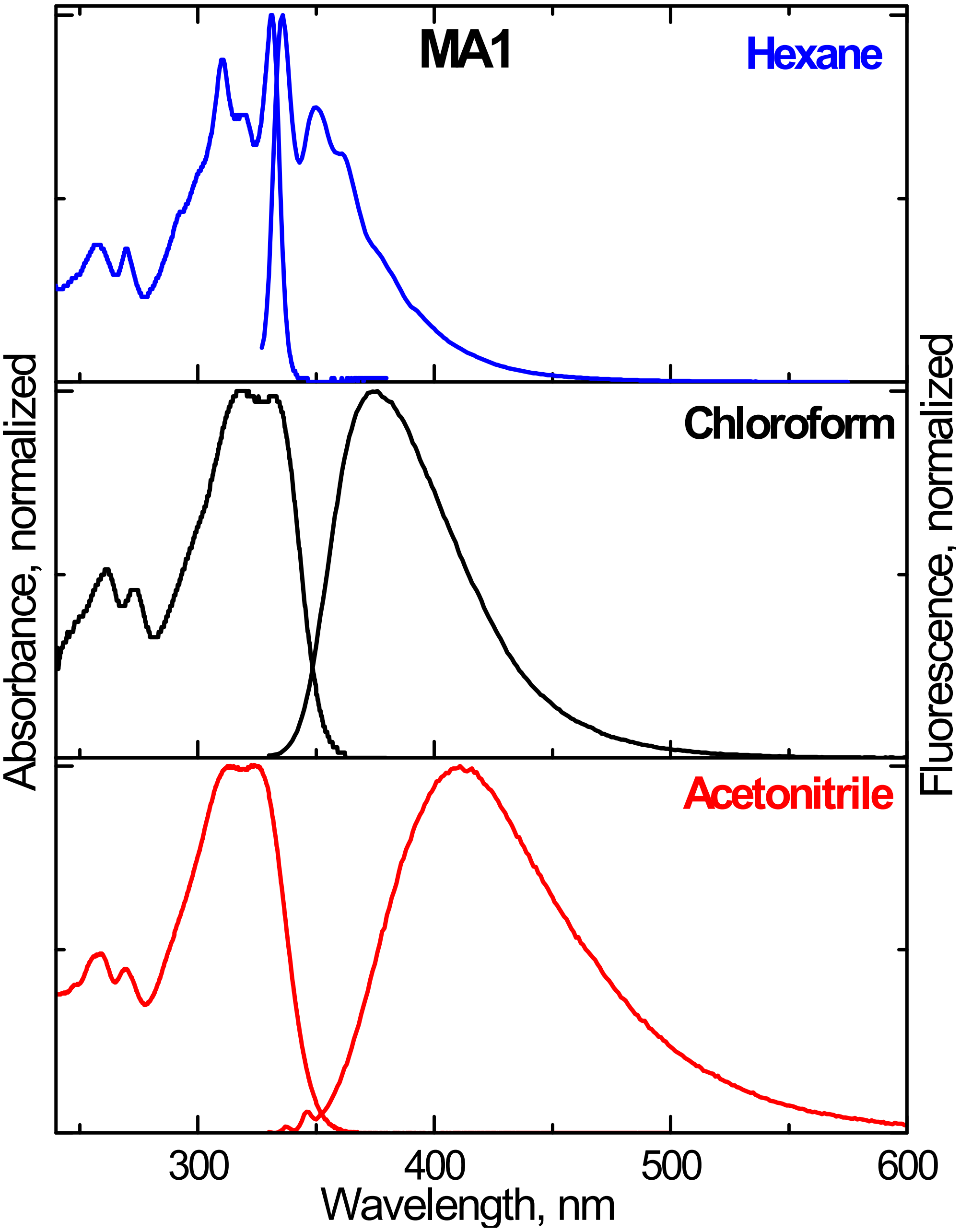


Figure S2 Steady state absorption and emission spectra of **MA1** in *n*-hexane (blue), chloroform (black) and acetonitrile (red) at room temperature.

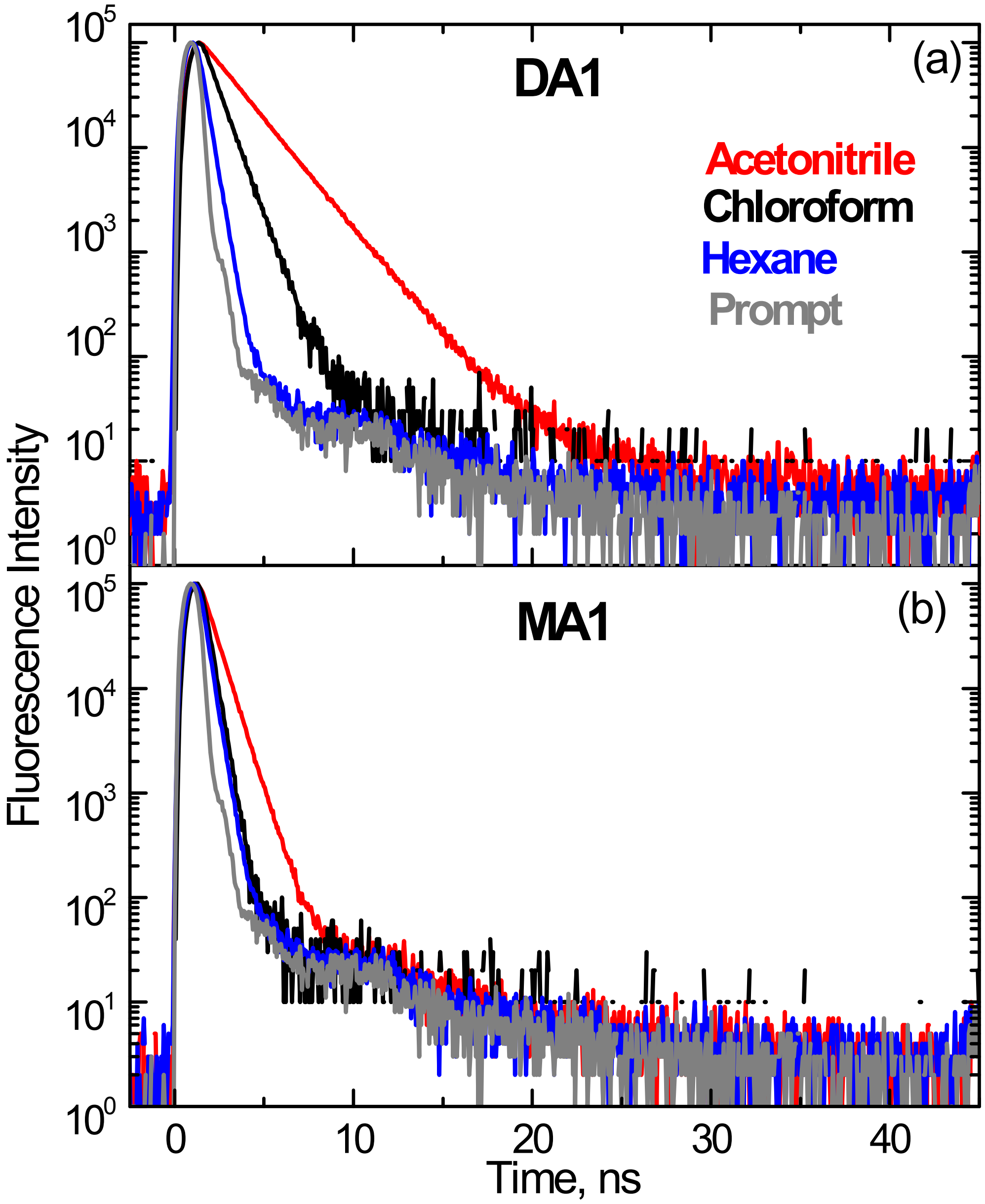


Figure S3 Fluorescence decay profiles of **DA1**(a) and **MA1**(b) in *n*-hexane (blue), chloroform (black) and acetonitrile (red) at room temperature obtained by exciting at 335 nm nano LED sources.

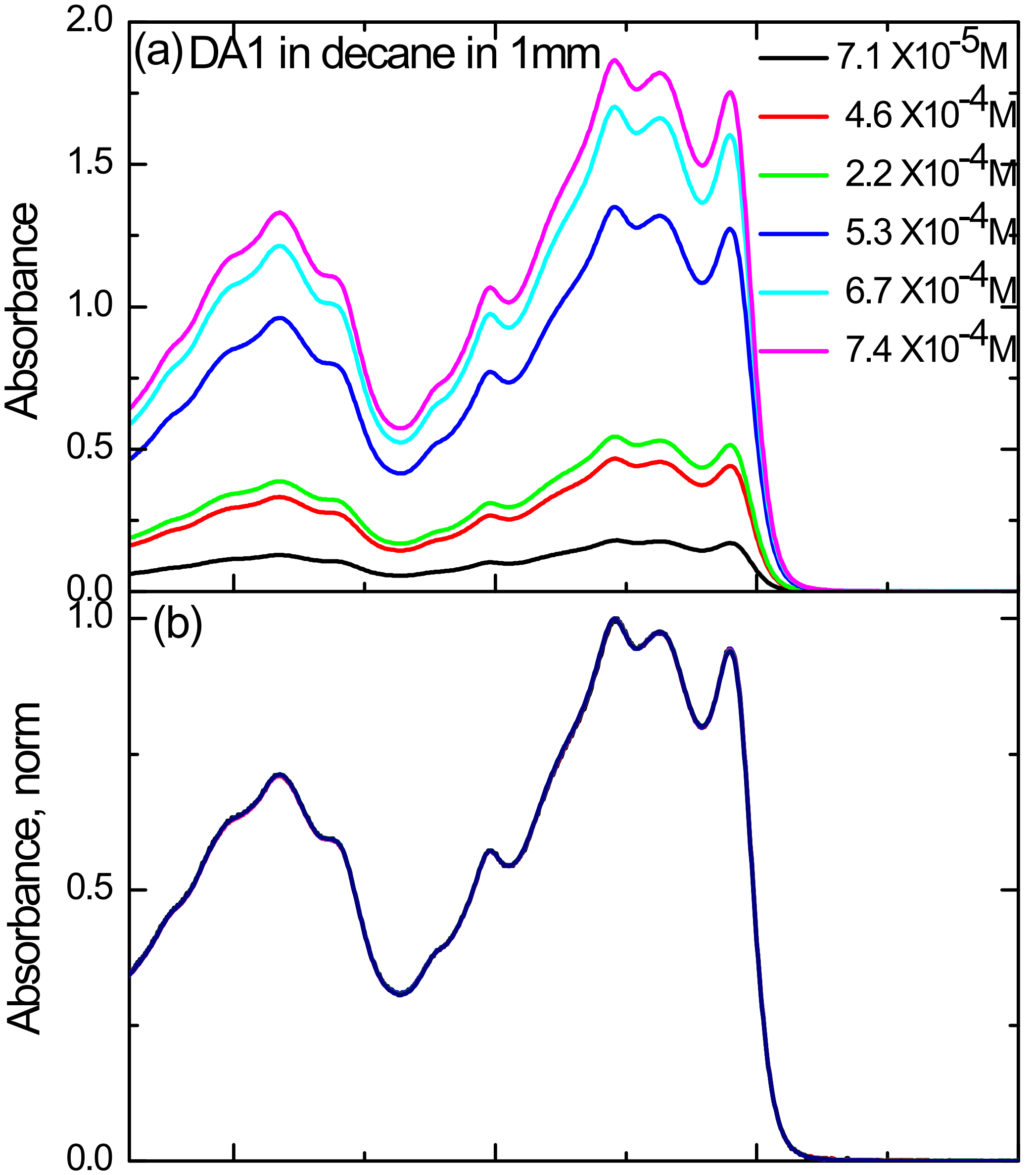


Figure S4. (a) Absorption spectra of DA1 in decane with increase of concentration from 7.1 ×10^{-5} M to 7.4 × 10^{-4} M measured in 1 mm pathlength. (b) Normalized absorption spectra of the above mentioned concentrations showed no significant change in the spectral pattern with increase of concentration.

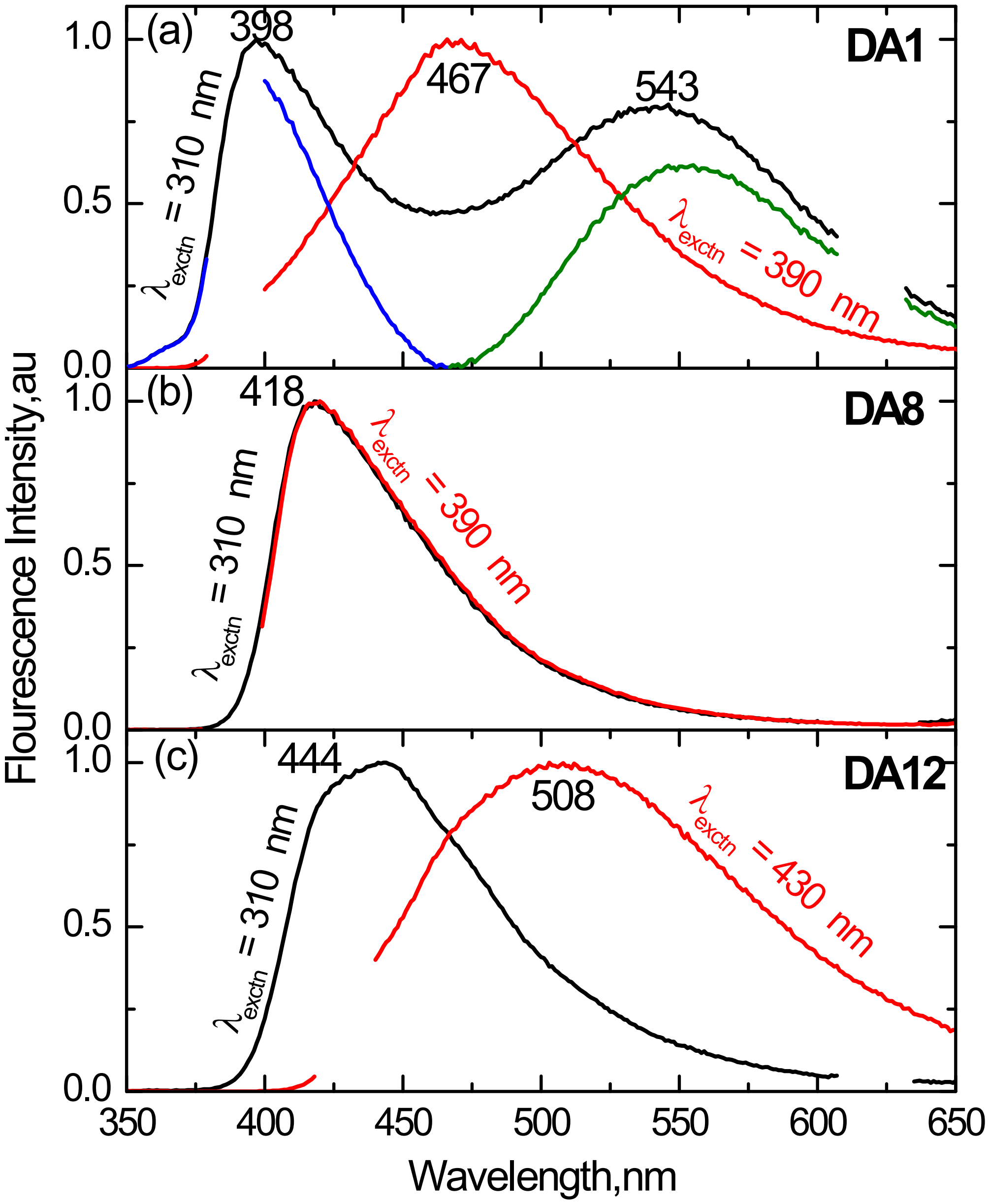


Figure S5 Normalized fluorescence spectra of **DA** derivatives. The emission maximum and excitation wavelength are given. The differential fluorescence spectra (blue and green) are obtained by subtracting the spectra obtained by exciting at 390 nm from 310 nm.

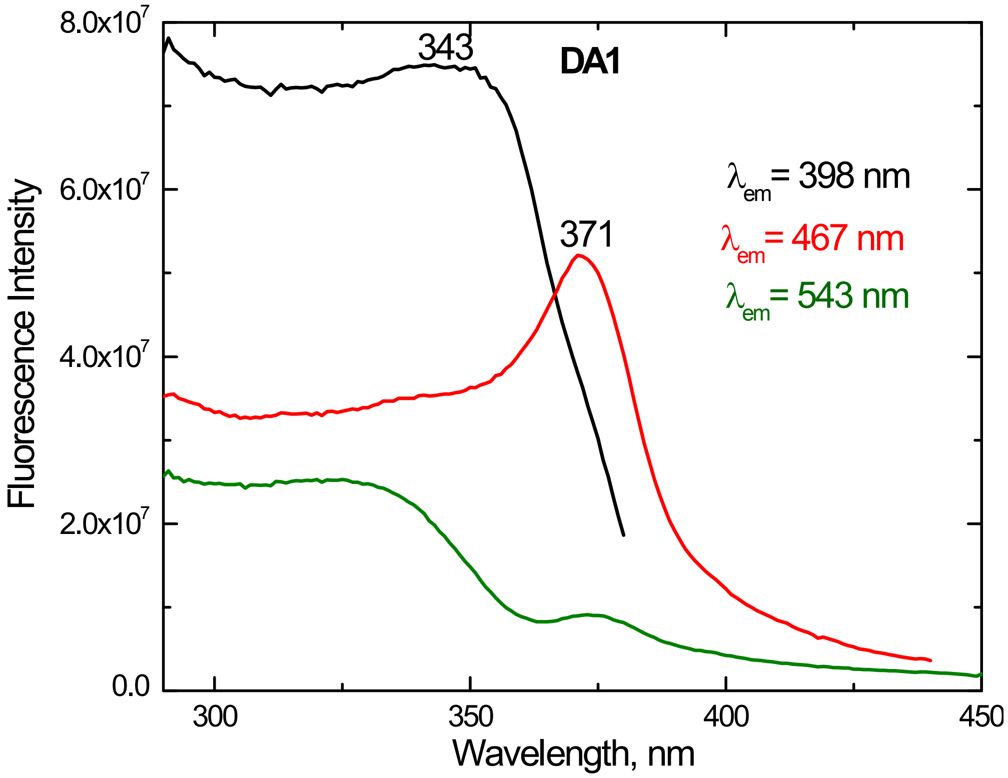


Figure S6 Solid state excitation spectra of **DA1** prepared by fast precipitation by monitoring emission at different wavelength mentioned in the insets.

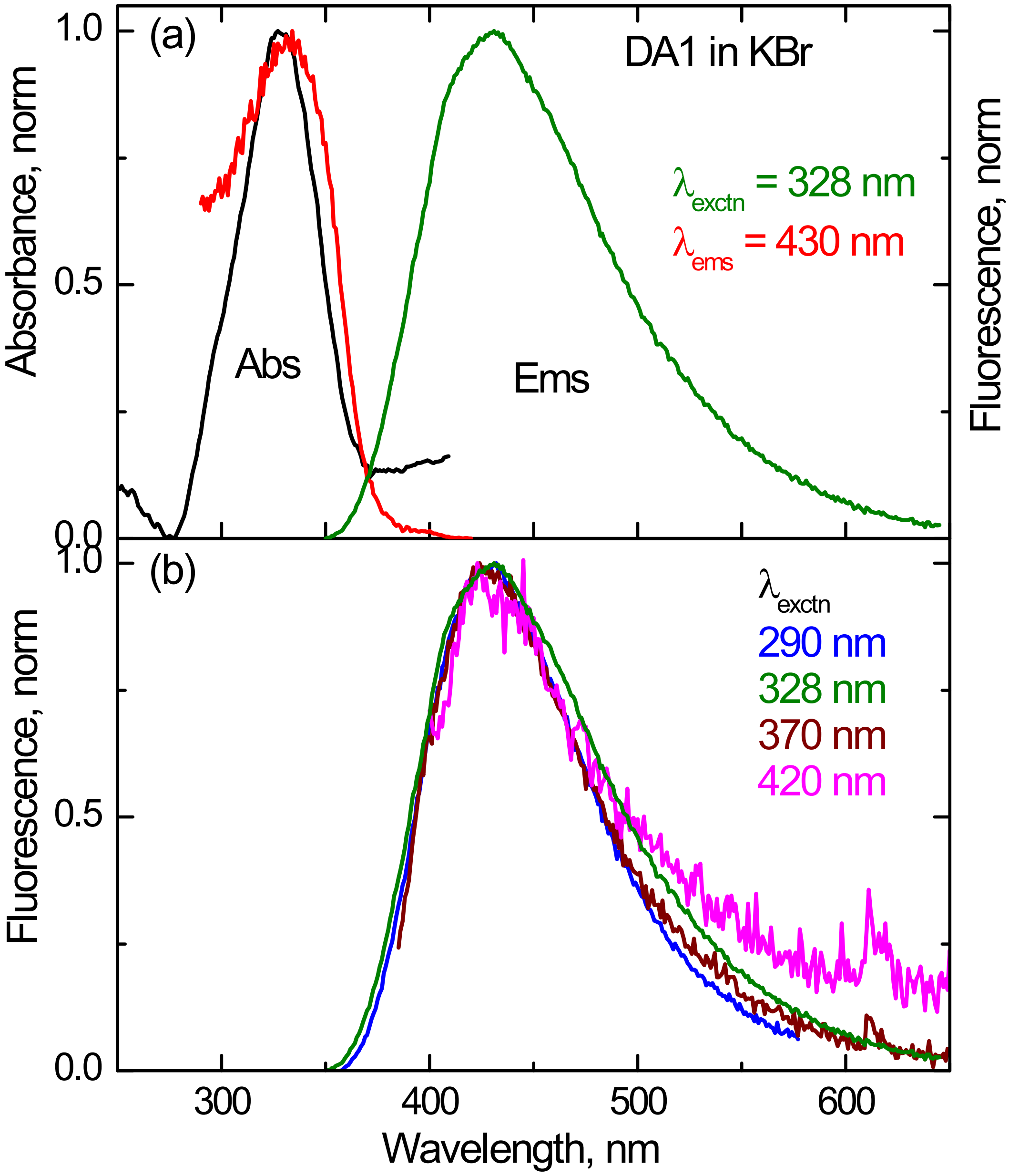


Figure S7 (a) Absorption, emission and excitation spectra of DA1 in KBr (0.002%). (b) Emission spectra obtained by exciting at different wavelength.

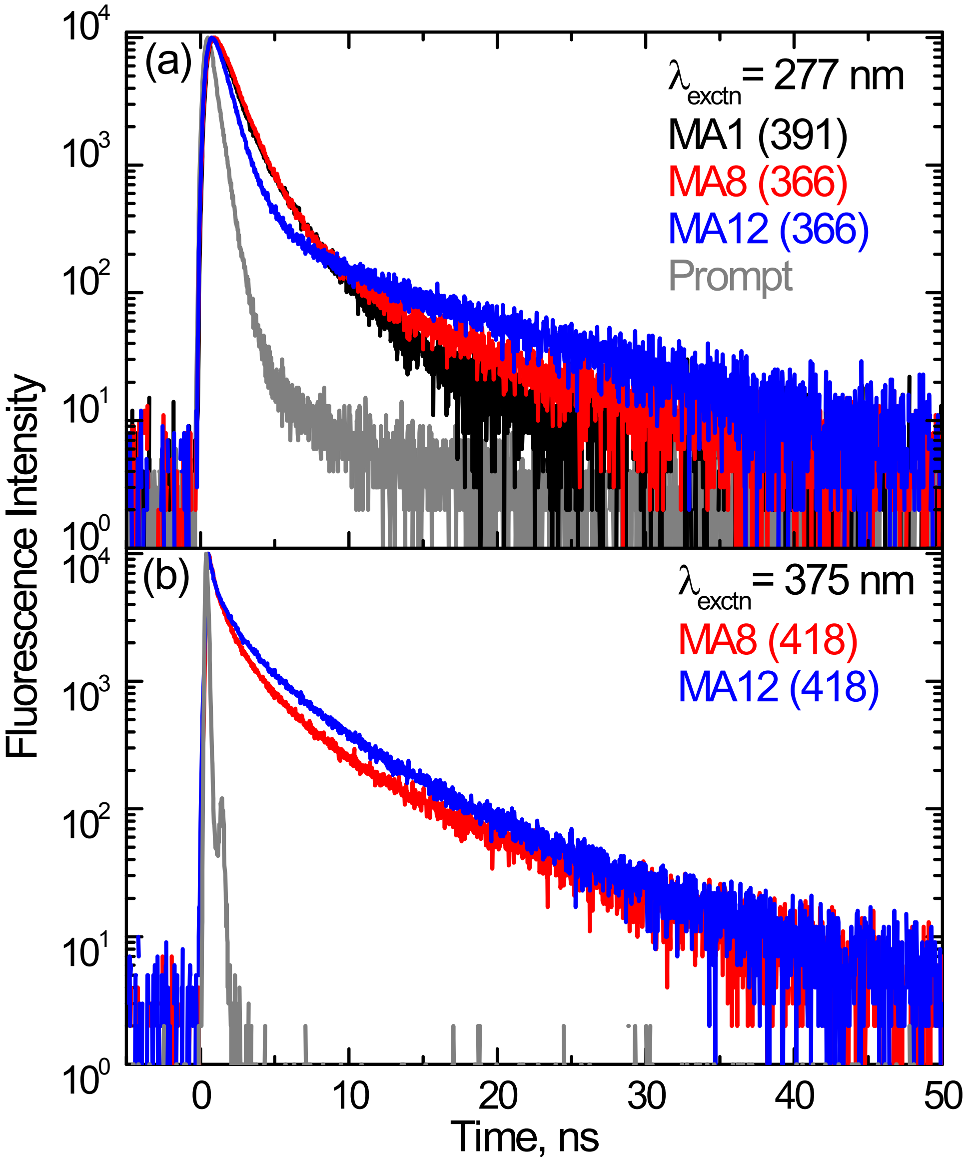


Figure S8 Solid state fluorescence decay profiles of **MA** derivatives obtained by exciting at 277(a) and 375(b) nm. The materials of **MA1**, **MA8** and **MA12** are given black, red and blue colours respectively. The probing wavelength in nm is given in the bracket.

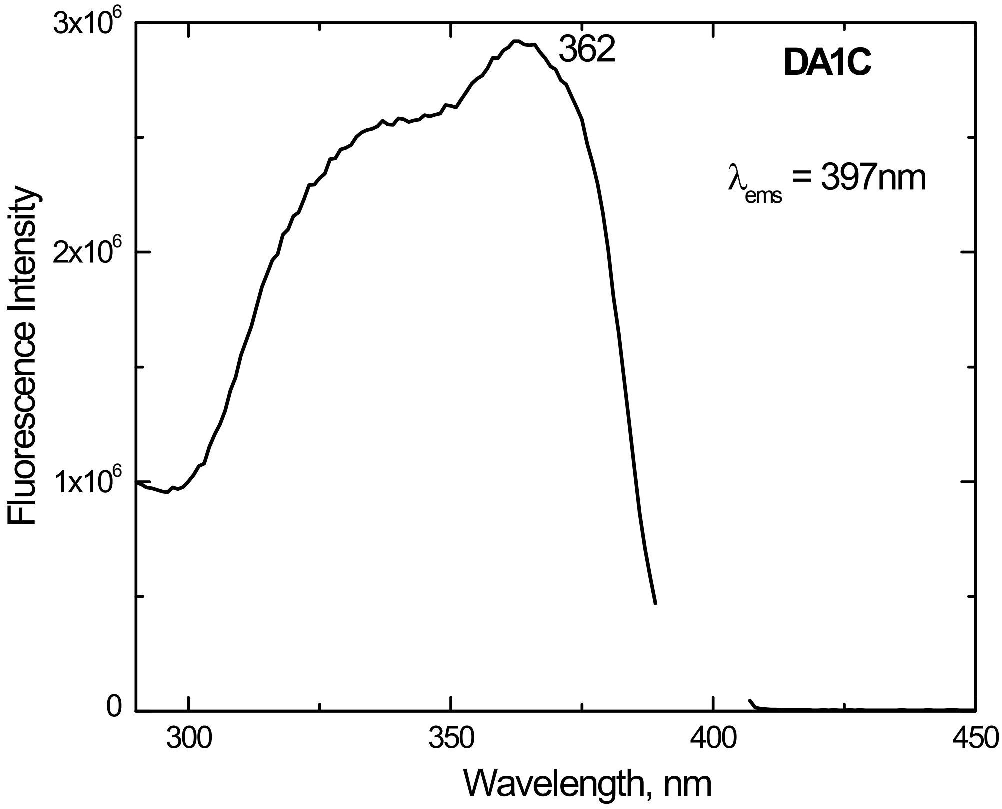


Figure S9 Solid state excitation spectra of **DA1C** prepared by slow crystallization by monitoring emission at 397nm mentioned in the insets.

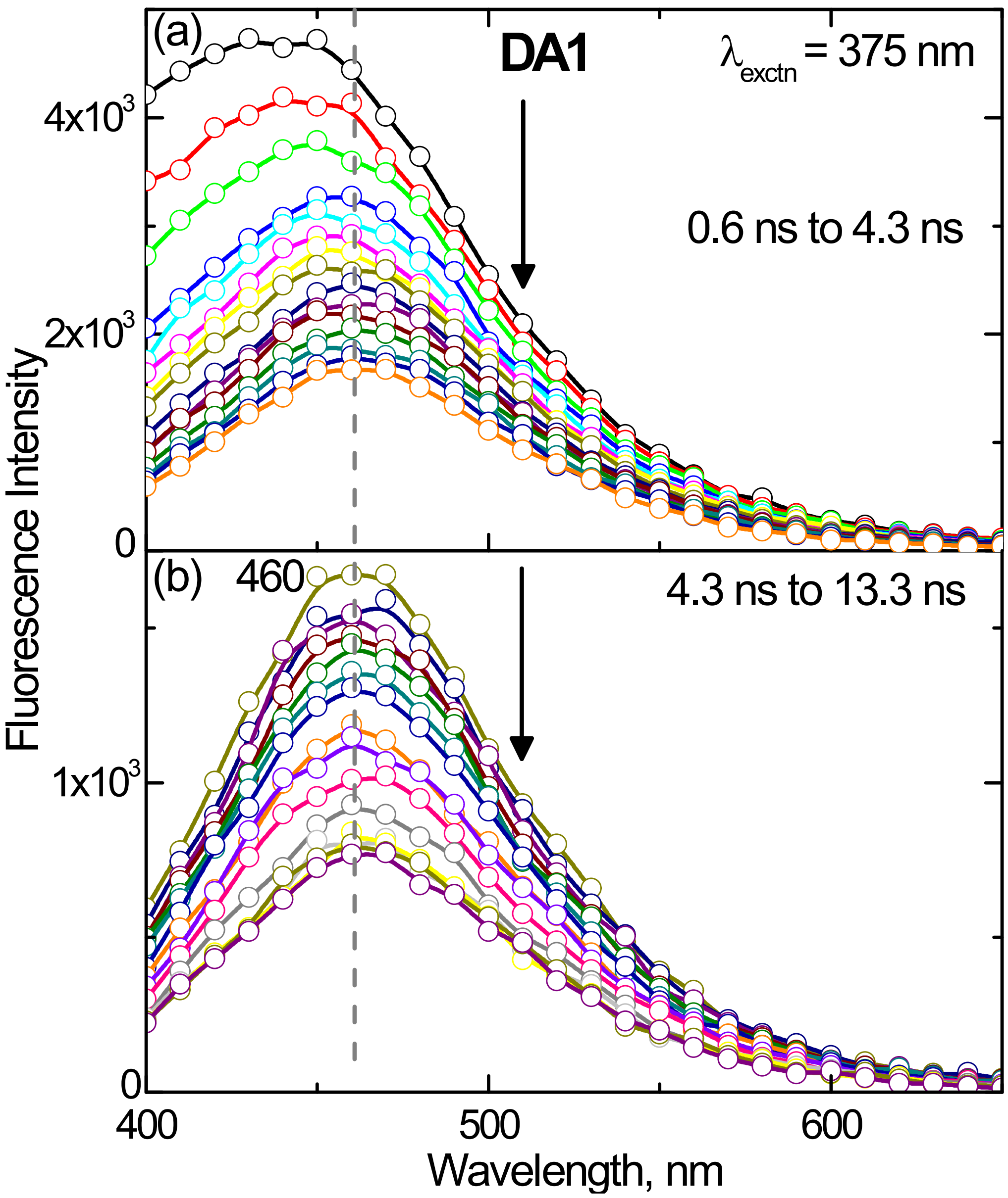


Figure S10 (a) Time-resolved emission spectra of **DA1** materials recorded from 0.6 to 4.3 ns. (b) From 4.3 to 13.3 ns. The excitation wavelength is 375 nm.

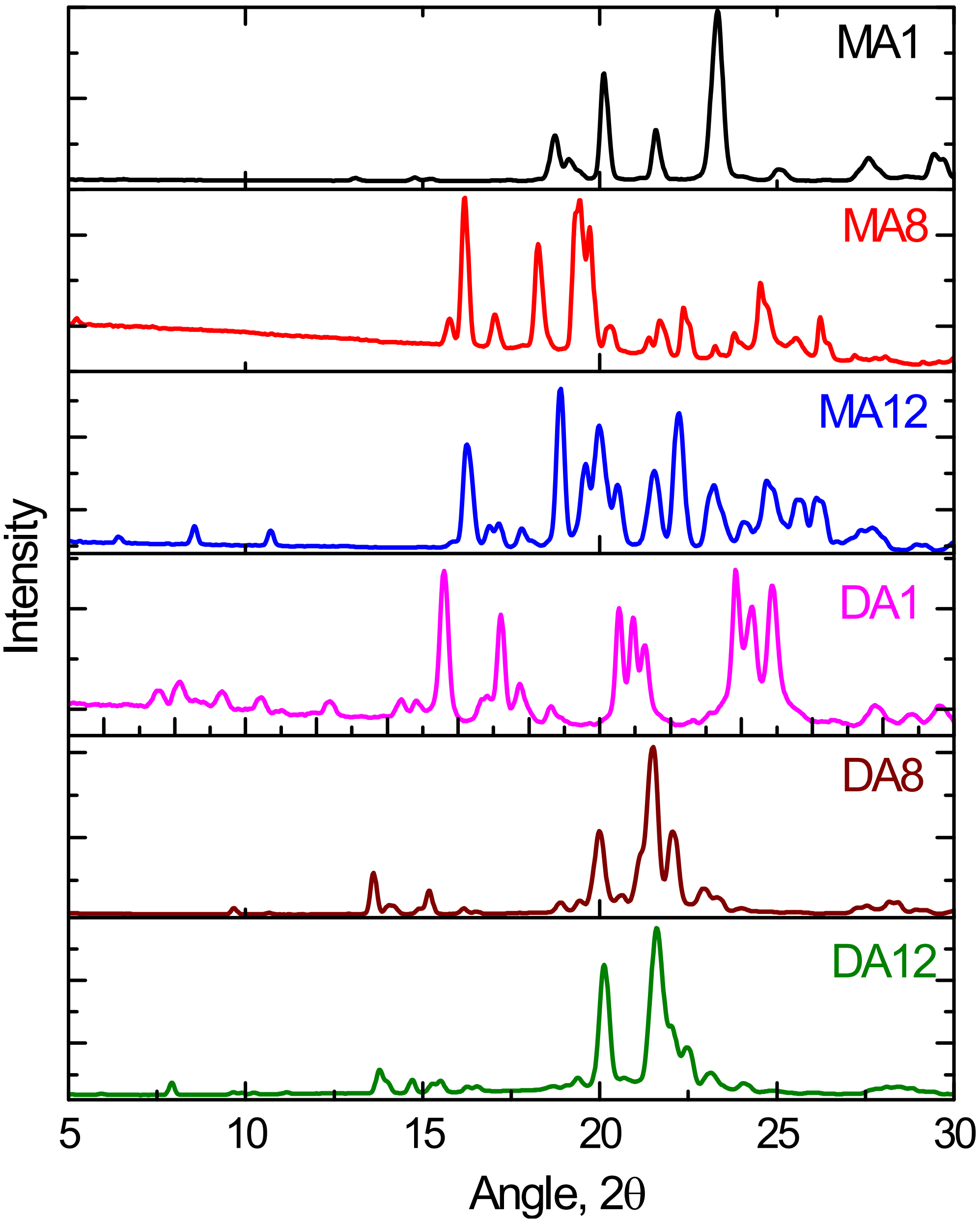


Figure S11 Powder XRD pattern of all the derivatives.

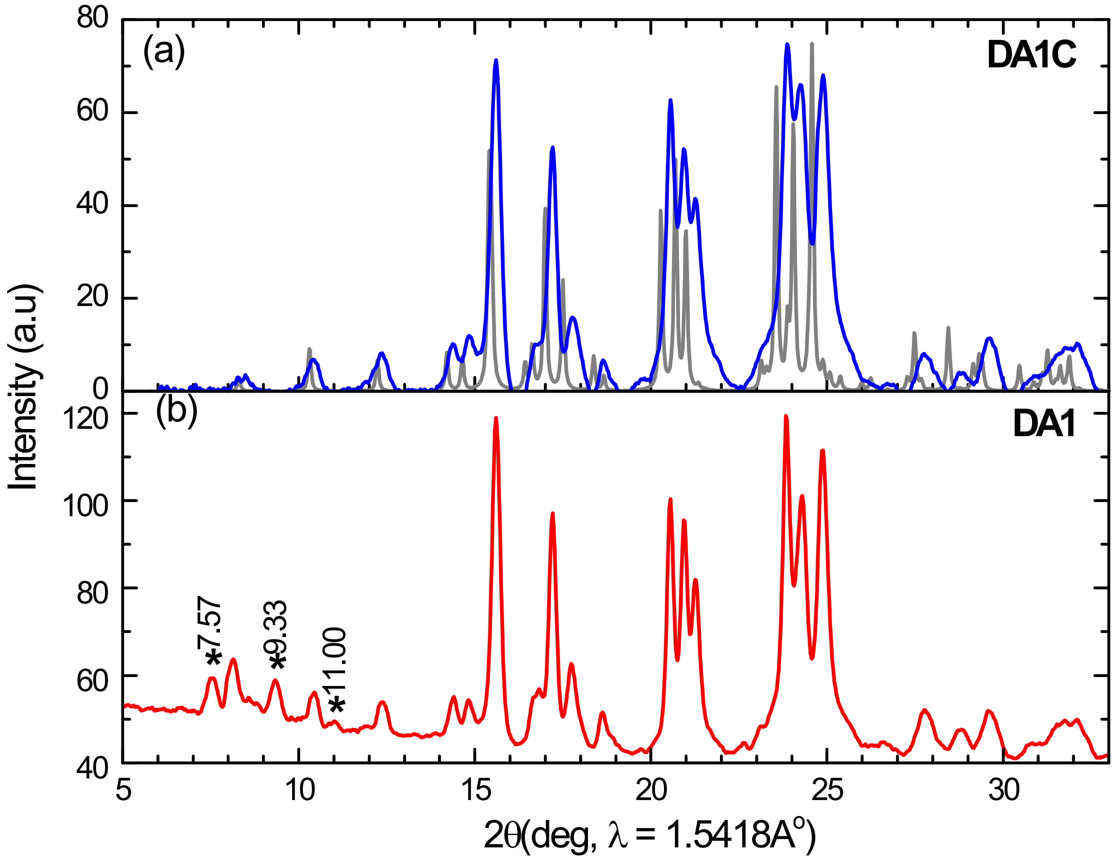
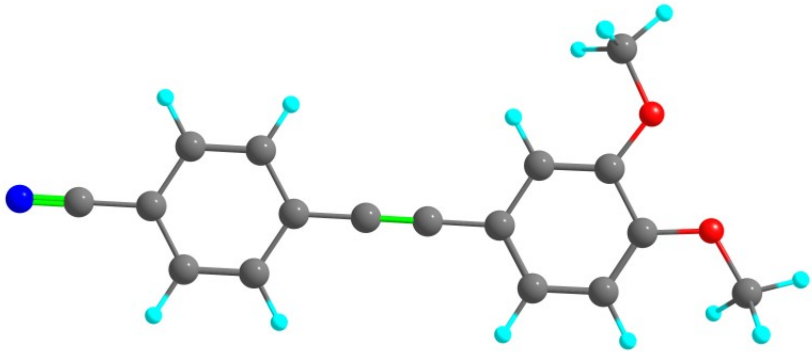


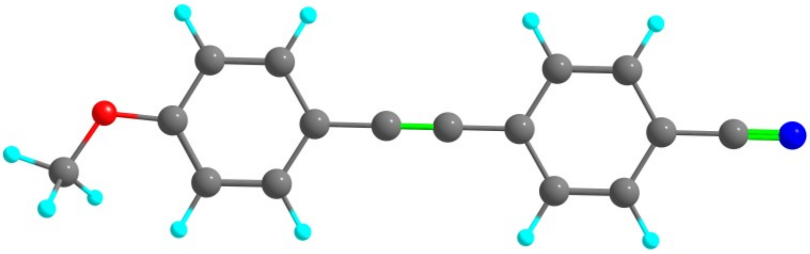
Figure S12 (a) The experimental powder X-ray diffraction pattern of crushed **DA1C** (blue) and simulated from single crystal structure (grey). (b) The presence of new additional peaks in **DA1** are shown with asterisk, viz., 7.57 (11.7Å), 9.33 (9.5Å) and 11.00 (8.06Å).

Key optimized structures and theoretical data of **DA1** by CAM B3LYP/6-31G(d)



6	1.370161000	-0.070162000	0.000000000
6	1.727390000	-1.440362000	0.000000000
6	2.383991000	0.896118000	0.000000000
1	0.938290000	-2.181974000	0.000000000
1	2.122696000	1.949024000	0.000000000
6	3.059920000	-1.828449000	0.000000000
6	3.725941000	0.511088000	0.000000000
1	4.495092000	1.274638000	0.000000000
6	4.080474000	-0.838106000	0.000000000
6	-5.252019000	1.776221000	0.000000000
6	-4.898651000	0.414829000	0.000000000
6	-4.242573000	2.755685000	0.000000000
1	-5.678033000	-0.340406000	0.000000000
1	-4.516050000	3.805950000	0.000000000
6	-3.562569000	0.041978000	0.000000000
6	-2.907195000	2.380297000	0.000000000
1	-3.290774000	-1.008535000	0.000000000
1	-2.129072000	3.136516000	0.000000000
6	-2.541283000	1.016708000	0.000000000
6	-1.173593000	0.633854000	0.000000000
6	0.000000000	0.309459000	0.000000000
6	-6.630950000	2.162614000	0.000000000
7	-7.751770000	2.476485000	0.000000000
8	3.499490000	-3.116017000	0.000000000
6	2.528548000	-4.150289000	0.000000000
1	1.893688000	-4.107622000	0.894996000
1	1.893688000	-4.107622000	-0.894996000
1	3.091123000	-5.085390000	0.000000000
8	5.352396000	-1.311846000	0.000000000
6	6.416837000	-0.372715000	0.000000000
1	7.333622000	-0.964426000	0.000000000
1	6.393226000	0.262376000	-0.895216000
1	6.393226000	0.262376000	0.895216000

Key optimized structures and theoretical data of **MA1 by CAM B3LYP/6-31G(d)**



6	-4.364590000	1.168877000	-0.000017000
6	-2.977909000	1.206706000	-0.000419000
6	-5.037469000	-0.066173000	0.000220000
1	-2.459418000	2.159878000	-0.000599000
6	-2.223903000	0.013317000	-0.000595000
6	-4.295862000	-1.261207000	0.000021000
1	-4.815890000	-2.213776000	0.000193000
6	-2.909245000	-1.220795000	-0.000383000
1	-2.337791000	-2.143208000	-0.000532000
1	-4.937487000	2.090607000	0.000121000
6	-0.803932000	0.053786000	-0.000954000
6	0.413015000	0.087941000	-0.001015000
6	1.834099000	0.131185000	-0.000609000
6	2.522171000	1.365664000	-0.000194000
6	2.593269000	-1.052608000	-0.000606000
1	1.952472000	2.289693000	-0.000210000
1	2.081042000	-2.009813000	-0.000904000
6	3.905606000	1.406889000	0.000259000
6	3.985526000	-1.018665000	-0.000156000
1	4.440594000	2.351202000	0.000635000
1	4.538650000	-1.950697000	-0.000247000
6	4.650538000	0.215339000	0.000262000
8	6.002234000	0.366201000	0.000684000
6	-6.469031000	-0.106857000	0.000679000
7	-7.632464000	-0.140164000	0.001306000
6	6.814443000	-0.799721000	0.000864000
1	6.640903000	-1.410180000	-0.894605000
1	7.845870000	-0.443722000	0.001390000
1	6.640089000	-1.410516000	0.895992000

Table ST1 Absorption and fluorescence maxima, quantum yield, lifetime, radiative and non-radiative rate constants of **MA8** in various solvents

Solvents	**Dielectric constant, ε**	**Refractive index, n**	**Absorption max (λ_{max}), nm**	**Fluorescence max (λ_{max}) nm**	**Stokes shift, Δν cm^{-1}**	**Fluorescence quantum yield, Φ_f**	**Fluorescence lifetime (τ), ns**	**Radiative constant, ($K_{r)}$, 10^9 s^{-1}**	**Non radiative constant, ($K_{nr)}$, 10^9 s^{-1}**
n-hexane	1.88	1.3723	313, 334	337	267	0.18	0.34	0.52	2.42
n-heptane	1.92	1.3851	313, 334	337	267	0.16	0.36	0.44	2.34
1,4-dioxane	2.21	1.4203	317, 331	370	3,184	0.11	0.36	0.31	2.51
Chloroform	4.89	1.442	321, 334	378	3,485	0.17	0.43	0.39	1.96
Ethyl acetate	6.02	1.3698	316, 330	379	3,918	0.09	0.40	0.22	2.28
Dichloromethane	9.08	1.4242	320, 332	389	4,414	0.14	0.54	0.26	1.59
1-propanol	20.1	1.387	319, 330	397	5,114	0.17	0.64	0.27	1.29
Acetonitrile	35.94	1.341	317, 325	414	6,615	0.10	0.83	0.12	1.08
Dimethyl sulphoxide	46.45	1.477	321, 330	417	6,322	0.17	1.17	0.14	0.71

Fluorescence lifetimes were obtained by exciting at 335 nm and χ^2 value of fluorescence kinetics fit is between 1.0 to 1.2..

Table ST2 Absorption and fluorescence maxima, quantum yield, lifetime, radiative and non-radiative rate constants of **DA8** in various solvents

Solvents	**Dielectric constant, ε**	**Refractive index, n**	**Absorption max (λ_{max}), nm**	**Fluorescence max (λ_{max}) nm**	**Stokes shift, $\Delta\nu$ cm^{-1}**	**Fluorescence quantum yield, Φ_f**	**Fluorescence lifetime, (τ), ns**	**Radiative constant, (K_r), 10^9 s^{-1}**	**Non radiative constant, (K_{nr}), 10^9 s^{-1}**
n-hexane	1.88	1.3723	324, 347	351	328	0.19	0.39	0.47	2.08
n-heptane	1.92	1.3851	325, 347	352	409	0.19	0.40	0.48	2.02
1,4-dioxane	2.21	1.4203	331	401	5,274	0.18	0.94	0.20	0.87
Chloroform	4.89	1.442	334	413	5,727	0.19	1.17	0.16	0.69
Ethyl acetate	6.02	1.3698	330	414	6,333	0.18	1.14	0.16	0.72
Dichloromethane	9.08	1.4242	334	426	6,829	0.26	1.60	0.16	0.47
1-propanol	20.1	1.387	332	428	6,756	0.12	0.94	0.13	0.94
Acetonitrile	35.94	1.341	330	458	8,469	0.15	2.07	0.07	0.41
Dimethyl sulphoxide	46.45	1.477	335	467	8,437	0.25	2.44	0.10	0.48

Fluorescence lifetimes were obtained by exciting at 335 nm and χ^2 value of fluorescence kinetics fit is between 1.0 to 1.2.

Table ST3 Absorption and fluorescence maxima, quantum yields, lifetime, radiative and non-radiative rate constants of **MA12** in various solvents

Solvents	Dielectric constant, ε	Refractive index, n	Absorption max (λ_{max}), nm	Fluorescence max (λ_{max}) nm	Stokes shift, $\Delta\nu$ cm^{-1}	Fluorescence quantum yield, Φ_f	Fluorescence lifetime, (τ), ns	Radiative constant, (K_r), 10^9 s^{-1}	Non radiative constant, (K_{nr}), 10^9 s^{-1}
n-hexane	1.88	1.372	313, 334	338	354	0.16	0.34	0.45	2.45
n-heptane	1.92	1.385	313, 334	338	354	0.17	0.35	0.49	2.37
1,4-dioxane	2.21	1.420	316, 332	371	3,166	0.11	0.35	0.33	2.53
Chloroform	4.89	1.442	322, 334	378	3,485	0.14	0.43	0.37	2.02
Ethyl acetate	6.02	1.369	316, 330	378	3,848	0.09	0.41	0.23	2.24
Dichloromethane	9.08	1.424	320, 332	389	4,414	0.14	0.53	0.26	1.62
1-propanol	20.1	1.387	320, 329	398	5,270	0.13	0.65	0.21	1.34
Acetonitrile	35.94	1.341	317, 326	414	6,520	0.10	0.84	0.19	1.08
Dimethyl sulphoxide	46.45	1.477	322, 330	420	6,494	0.22	1.18	0.19	0.66

Fluorescence lifetimes were obtained by exciting at 335 nm and χ^2 value of fluorescence kinetics fit is between 1.0 to 1.2..

Table ST4 Absorption and fluorescence maxima, quantum yield, lifetime, radiative and non-radiative rate constants of **DA12** in various solvents

Solvents	**Dielectric constant, ε**	**Refractive index, n**	**Absorption max (λ_{max}), nm**	**Fluorescence max (λ_{max}) nm**	**Stokes shift, Δν cm^{-1}**	**Fluorescence quantum yield, Φ_f**	**Fluorescence lifetime, (τ), ns**	**Radiative constant, (K_r) , 10^9 s^{-1}**	**Non radiative constant, (K_{nr}), 10^9 s^{-1}**
n-hexane	1.88	1.3723	325, 347	351	328	0.19	0.39	0.48	2.05
n-heptane	1.92	1.3851	325,347	352	409	0.21	0.41	0.52	1.92
1,4-dioxane	2.21	1.4203	332	402	5245	0.20	0.93	0.22	0.86
Chloroform	4.89	1.442	335	413	5638	0.21	1.16	0.18	0.68
Ethyl acetate	6.02	1.3698	331	413	5998	0.21	1.14	0.18	0.70
Dichloromethane	9.08	1.4242	334	426	6466	0.25	1.58	0.16	0.47
1-propanol	20.1	1.387	332	432	6972	0.13	0.95	0.14	0.91
Acetonitrile	35.94	1.341	330	458	8469	0.16	2.07	0.08	0.40
Dimethyl sulphoxide	46.45	1.477	335	467	8437	0.25	2.43	0.10	0.31

Fluorescence lifetimes were obtained by exciting at 335 nm and χ^2 value of fluorescence kinetics fit is between 1.0 to 1.2.

Table ST5 Crystal data of **DA1**

S. No.	Carbon	Hydrogen	Oxygen	Distance (Å)	Distance (Å)	Distance (Å)	Angle (°)
1	1 C(2)	H(2)	O(13)	0.93	2.82	3.644(5)	149
2	1 C(2)	H(2)	O(14)	0.93	2.46	3.311(4)	153
3	1 C(3)	H(3)	N(7)	0.93	2.94	3.813(6)	157
5	1 C(15)	H(15)	O(14)	0.93	2.78	3.706(5)	173
6	1 C(16)	H(16A)	N(7)	0.96	3.04	3.975(7)	164
7	1 C(16)	H(16B)	O(13)	0.96	2.91	3.654(6)	135
9	1 C(17)	H(17B)	N(7)	0.96	2.70	3.509(6)	142