

Dicyanodistyrylbenzene based positional isomers: A comparative study of AIEE and stimuli responsive multicolour fluorescence switching

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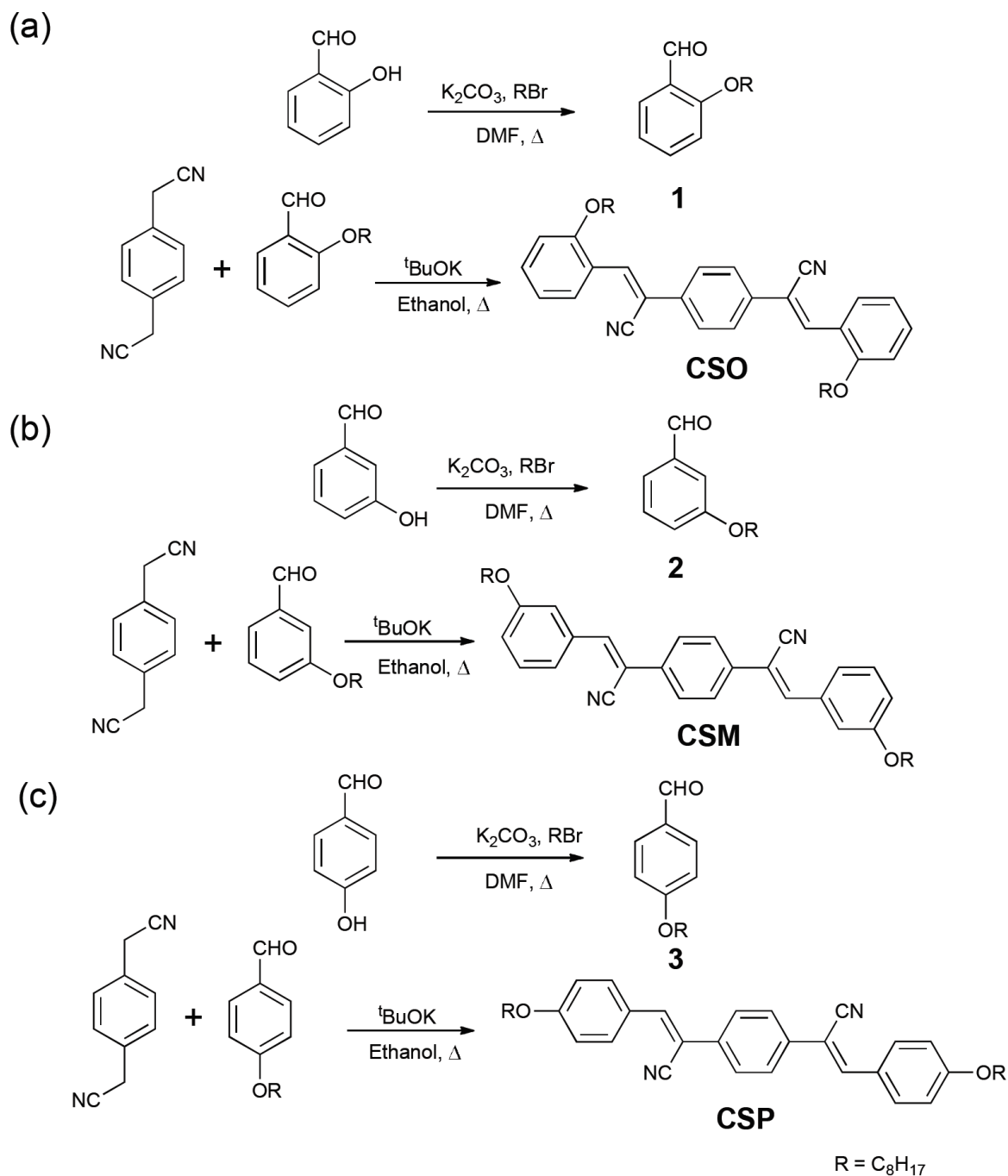
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section

All chemicals and solvents required for the synthesis and photophysical studies were purchased from Sigma Aldrich, Alfa Aesar and TCI and used without further purification. The ¹H NMR spectra and ¹³C NMR spectra were obtained from a Bruker Avance 400MHz spectrometer operating at temperature 25^oC. Fluorescence spectra were obtained using Horiba-Jobin-Yvon Fluorolog-3-11 Spectrofluorimeter. The quantum yield was measured on EDINBURGH FLS 1000 instrument attached with integrating sphere. The time resolved fluorescence lifetime experiments were performed on a time correlated single photon counting system (TCSPC) Fluorocube (Horiba-Jobin-Yvon). The powder X-ray diffractograms were recorded on Pananalytical Aeris Research and Bruker D8 discover (Temperature-dependent XRD) diffractometers. The single crystal X-ray data were collected from a Bruker D8 Venture (**CSO**) and Bruker D8 Quest Eco (**CSM** and **CSP**) single crystal X-ray diffractometers, and mass of the compounds were collected from a Thermo Fischer Scientific Exactive mass spectrometer.



Scheme S1: Synthetic route to octylated dicyanodistyrylbenzene derivatives **CSO**, **CSM** and **CSP**.

Synthesis of compounds **CSO**, **CSM** and **CSP**.

The different isomeric dicyanodistyrylbenzene derivatives were synthesized adopting the method in scheme S1.

1. General method for the synthesis of octyloxy substituted benzaldehydes.

Octyloxy substituted benzaldehydes were prepared by adopting the previously reported procedure.¹ Corresponding hydroxy benzaldehydes(20mmol),K₂CO₃(30mmol), and 1-bromo octane(20 mmol) were stirred at 80 °C in DMF under inert atmosphere for 12 hours. The

reaction mixtures were evaporated and the organic phase was extracted with DCM and washed with water. The organic phase in all the cases were column chromatographed over silica gel using ethyl acetate/hexane (1:9) to obtain the target compounds as oily liquids. The products were characterized using ^1H NMR and ^{13}C NMR.

Compound 1: Yield: 73.24%, ^1H NMR (400MHz, CDCl_3) δ (ppm) 10.5(s, 1H), 7.83(s, 1H), 7.52(m, 1H), 7.00(m, 2H), 4.07(t, J=4Hz, 2H), 1.84(m, 2H), 1.49 (m, 2H) 1.30(m, 8H), 0.89(m, 3H). ^{13}C NMR: δ (ppm) 189.816, 161.601, 135.864, 128.164, 124.973, 120.435, 112.541, 68.576, 31.778, 29.291, 29.197, 29.094, 26.054, 22.627, 14.046

Compound 2: Yield: 80.73 %, ^1H NMR (400MHz, CDCl_3) δ (ppm) 9.97(s, 1H), 7.45(m, 1H), 7.38 (m, 1H) 7.17(m, 2H), 3.95(t, J=2Hz, 2H), 1.82(m, 2H), 1.44 (m, 2H), 1.31(m, 8H), 0.94(m, 3H). ^{13}C NMR: δ (ppm) 192.183, 159.773, 137.831, 129.972, 123.233, 121.951, 112.909, 68.359, 31.797, 29.314, 29.211, 29.140, 26.004, 22.638, 14.059.

Compound 3: Yield: 88.73 %, ^1H NMR (400MHz, CDCl_3) δ (ppm) 9.86(s, 1H), 7.82(d, 2H J=8Hz), 6.99(d, 2H, J=4Hz), 4.04(s, 2H), 1.82(m, 2H), 1.33 (m, 2H), 1.31(m, 8H), 0.89(m, 3H). ^{13}C NMR: δ (ppm) 190.666, 164.270, 131.923, 129.766, 114.737, 68.406, 31.777, 29.288, 29.190, 29.048, 25.951, 22.625, 14.053.

2. Synthesis of the dicyanodistyrylbenzenes CSO, CSM, and CSP

The three isomeric dicyanodistyrylbenzenes were synthesized using Knoevenagel condensation reaction¹ with phenylenediacetonitrile and the corresponding octyloxy benzaldehyde. Octyloxybenzaldehyde (3.66 mmol) was taken in an oven dried flask and dissolved in 18 ml ethanol. To this solution added 1,4-phenylene diacetonitrile (2 mmol) and $^t\text{BuOK}$ (2.8 mmol). The reaction mixture was stirred for 2 hrs at 80°C under inert atmosphere. The reaction mixture was filtered and washed with excess ethanol. The precipitate of CSO and CSP were purified by recrystallization from dioxane, whereas, CSM was recrystallized from dichloromethane. All of the dicyanodistyrylbenzene derivatives were characterized using ^1H NMR, ^{13}C NMR, HRMS (ESI) and single-crystal X-ray diffraction.

CSO: Yield: 60.32 % ^1H NMR(400MHz, CDCl_3) δ (ppm) 8.20(m, 2H), 8.07(s, 2H), 7.77(s, 4H), 7.42(M, 2H), 7.07 (m, 2H), 6.95(m, 2H), 4.05(s, 4H), 1.86(m, 4H), 1.50(m, 4H), 1.32(m, 16H), 0.87(m, 6H) ^{13}C NMR 152.89, 133.16, 130.61, 127.53, 123.75, 121.75, 118.19, 115.95, 113.28, 107.03, 105.53, 63.88, 27.03, 24.56, 24.52, 24.38, 21.40, 17.92, 9.36. HRMS (ESI)m/z 588.3785[M⁺]

CSM: Yield 72.14 % ¹H NMR (400MHz, CDCl₃) δ (ppm) 7.76(s, 4H), 7.57(s, 2H), 7.53(s, 2H), 7.51(s, 2H), 7.35(t, J=4Hz, 2H), 7.01(t, J=4Hz, 2H), 4.02(t, 4Hz, 4H), 1.82(m, 4H), 1.49(m, 4H), 1.32(m, 16H), 0.89(m, 6H). ¹³C NMR 154.74, 138.16, 130.45, 129.88, 125.24, 121.84, 117.39, 113.19, 112.98, 109.52, 105.90, 63.50, 27.08, 24.63, 24.51, 24.47, 21.32, 17.93, 9.38 **HRMS (ESI)** m/z 588.3818 [M⁺]

CSP :Yield: 76.93 % ¹H NMR (400MHz, CDCl₃) δ (ppm) 7.91(d, 4H, J=8Hz), 7.72 (s, 4H), 7.52(s, 2H), 6.98(q, 4H, J=6Hz), 3.98 (t, 4H, J=6Hz), 1.81(m, 4H), 1.57(m, 4H), 1.32(m, 16H), 0.89(t, 6H, J= 6Hz). ¹³C NMR 156.58, 137.51, 130.37, 126.67, 121.46, 121.32, 113.61, 110.20, 102.61, 63.54, 27.08, 24.60, 24.50, 24.39, 21.27, 17.93, 9.38. **HRMS (ESI)** m/z 588.3809[M⁺]

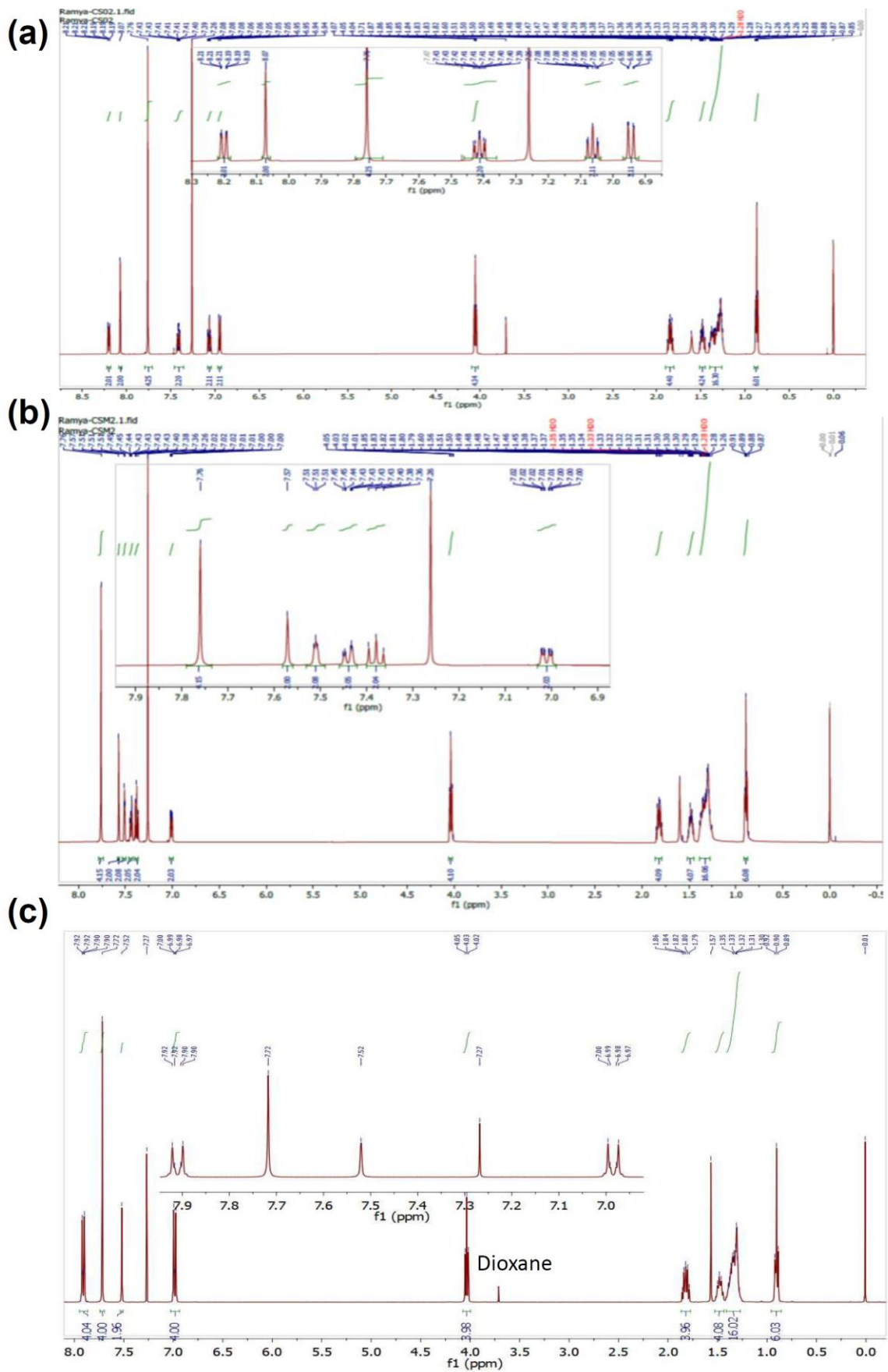


Fig. S1: ¹H NMR spectra of compounds (a) CSO (b) CSM and (c) CSP.

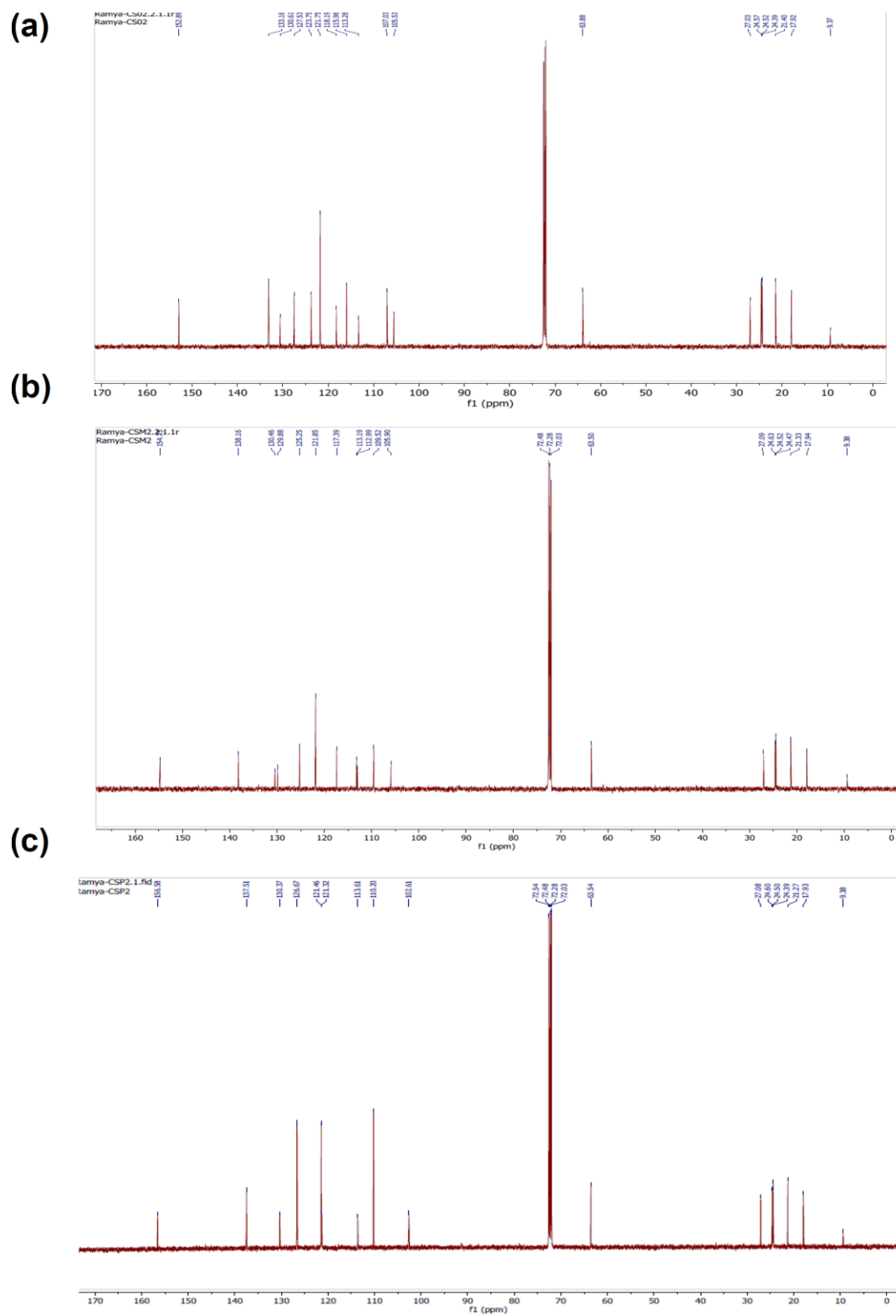


Table S1: Single crystal X-ray diffraction details for isomeric dicyanodistyrylbenzene derivatives.

Compound	CSO	CSM	CSP
Empirical Formula	C ₄₀ H ₄₈ N ₂ O ₂	C ₄₀ H ₄₈ N ₂ O ₂	C ₄₀ H ₄₈ N ₂ O ₂
Formula weight	588.80	588.80	588.80
Cell setting	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	P 2 ₁ /c
A (Å)	8.3073(3)	6.9341(3)	36.4315(17)
B (Å)	14.2311(5)	6.9886(3)	7.1569(3)
C (Å)	15.9393(6)	18.4291(10)	6.7041(3)
α (°)	65.653(2)	94.532(2)	90.000
β (°)	85.245(2)	93.486(2)	92.239(2)
γ (°)	78.854(2)	103.5810(10)	90.000
Cell volume (Å ³)	1684.40(11)	862.48 (7)	1746.67(13)
Z	2	1	2
F	636	318	636
ρ(Mg/m ³)	1.161	1.134	1.120
Crystal size (mm ³)	0.15 x 0.15 x 0.10	0.30 x 0.16 x 0.15	0.30 x 0.25 x 0.10
Index ranges	-9 ≤ h ≤ 9, -16 ≤ k ≤ 16, -18 ≤ l ≤ 18	-8 ≤ h ≤ 8, -8 ≤ k ≤ 8, -22 ≤ l ≤ 22	-35 ≤ h ≤ 45, -8 ≤ k ≤ 8, -5 ≤ l ≤ 8
Reflections collected	54338	6361	6862
Number of independent reflections	5910	3104	3435
R ₁	0.0522	0.0650	0.0650
wR ₂ (all)	0.1189	0.1614	0.1840
S	1.089	1.085	1.064
No. parameters	480	276	284
Max. eÅ ⁻³	0.274	0.147	0.194
CCDC No	2093665	2093664	2093666

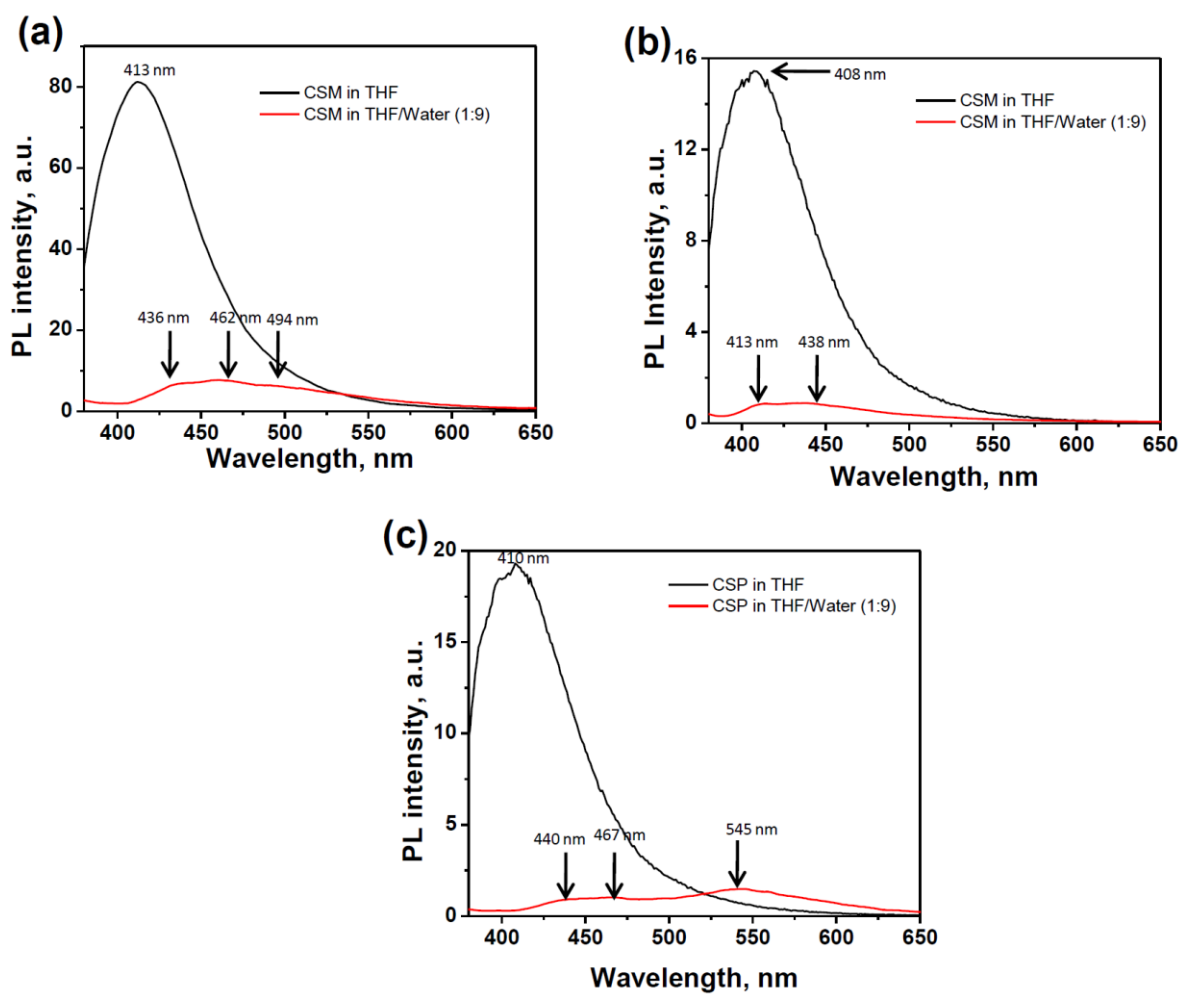


Fig. S3: Effect of water on aggregate formation in dicyadistyrylbenzene molecules (a) **CSO**, (b) **CSM** and (c) **CSP** (Concentration - $2.4 \times 10^{-6} \text{ML}^{-1}$).

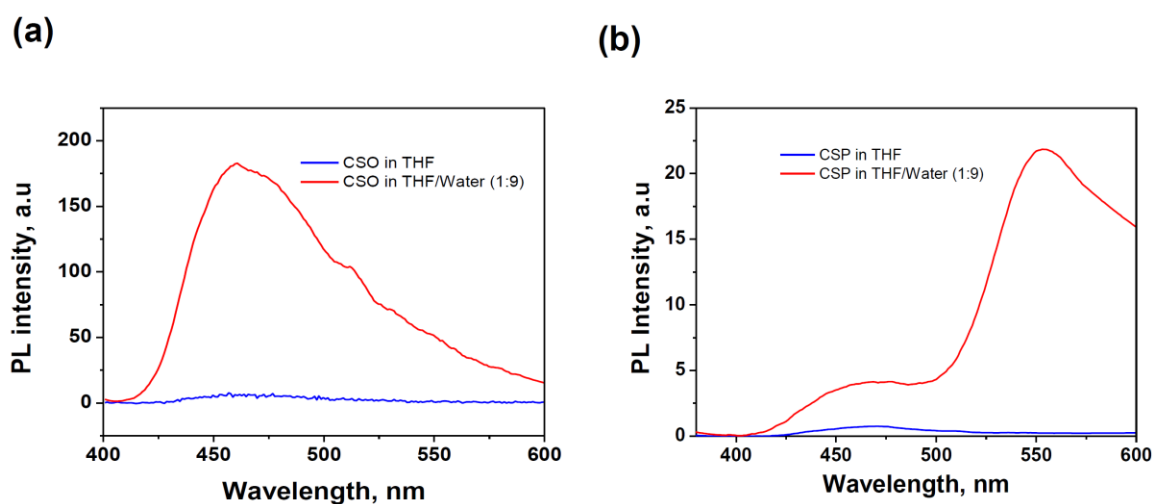


Fig. S4: Aggregation induced enhanced emission in THF/water mixture (1:9) (concentration $20 \times 10^{-6} \text{ML}^{-1}$) (a) **CSO** and (b) **CSP**.

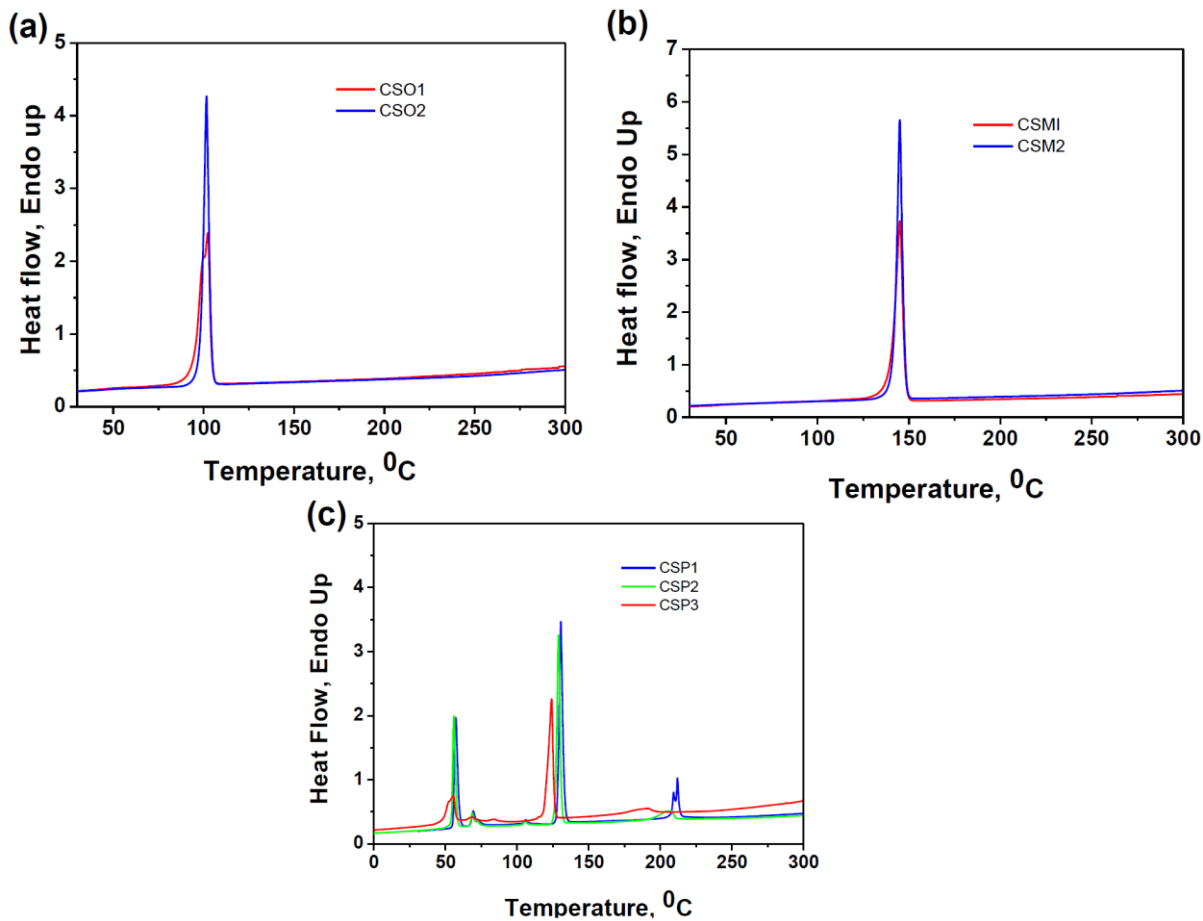


Fig. S5: First heating and cooling DSC curves of (a) **CSO**, (b) **CSM**, and (c) **CSP**

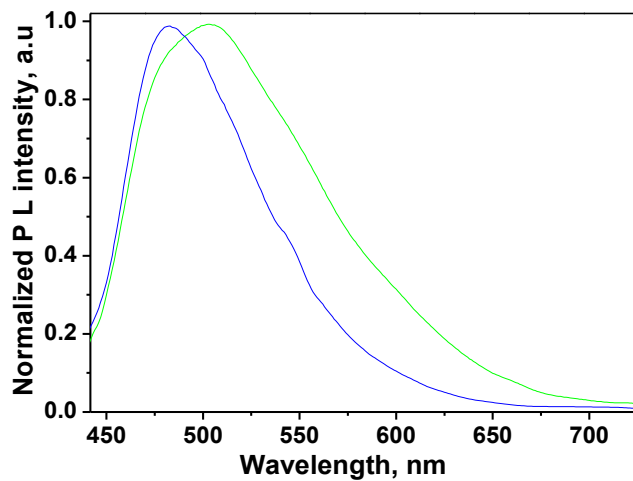


Fig. S6: Solvent recovered spectra of **CSP1** (blue line, from dioxane) and **CSP2** (green line, from DCM) from **CSP3**.

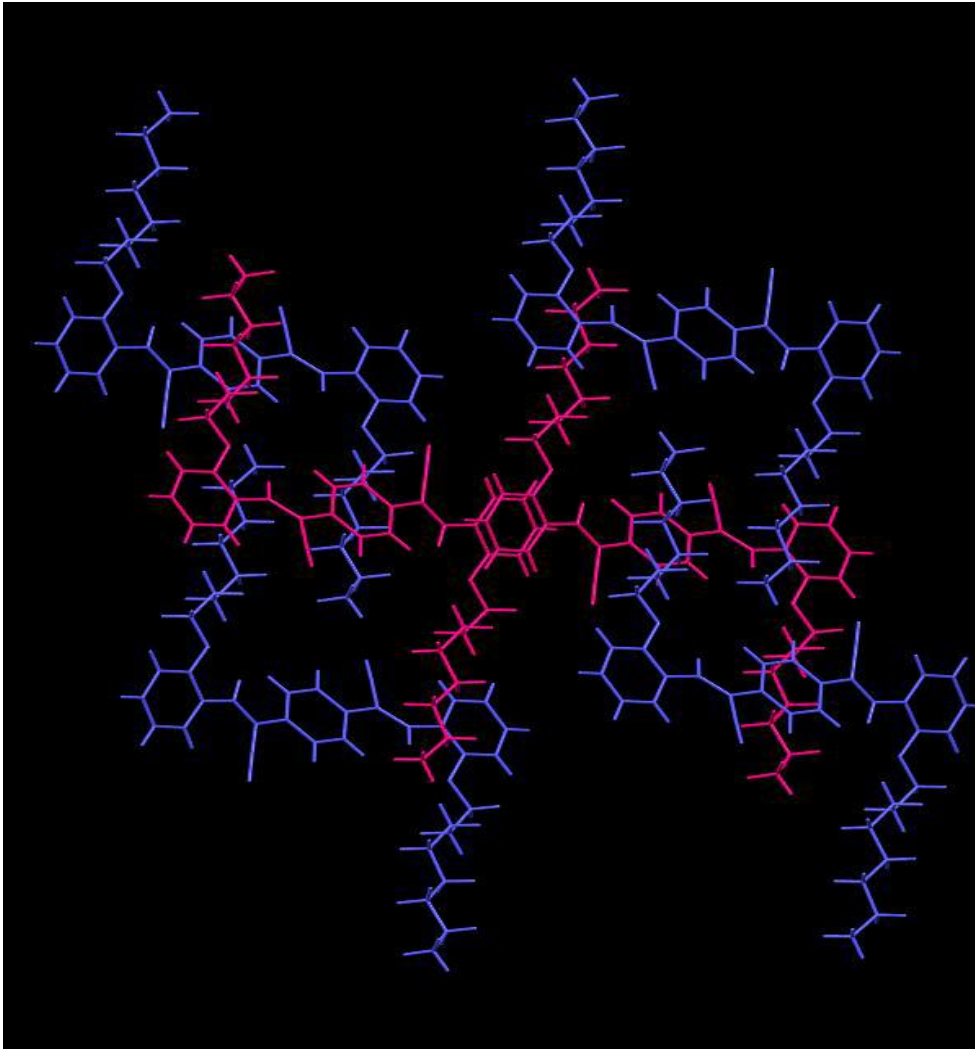


Fig. S7: Overlapping molecular pairs in crystal structure of **CSO1**

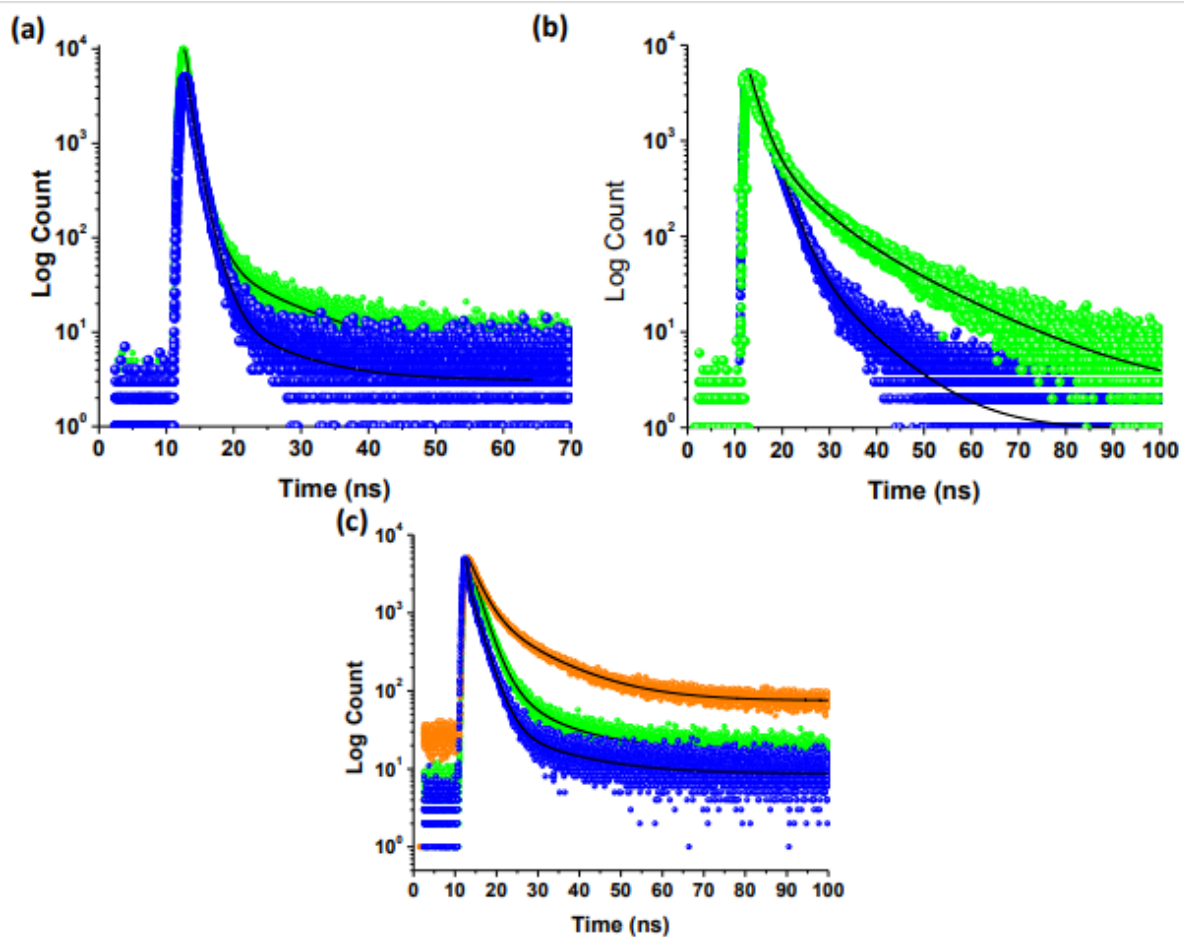


Fig. S8: Fluorescence decay profile for different forms of (a) **CSO** (**CSO1** (blue decay) and **CSO2** (green decay) (b) **CSM** (**CSM1** (blue decay) and **CSM2** (green decay) and (c) **CSP** (**CSP1**(blue decay), **CSP2** (green decay) and **CSP3** (orange decay)).

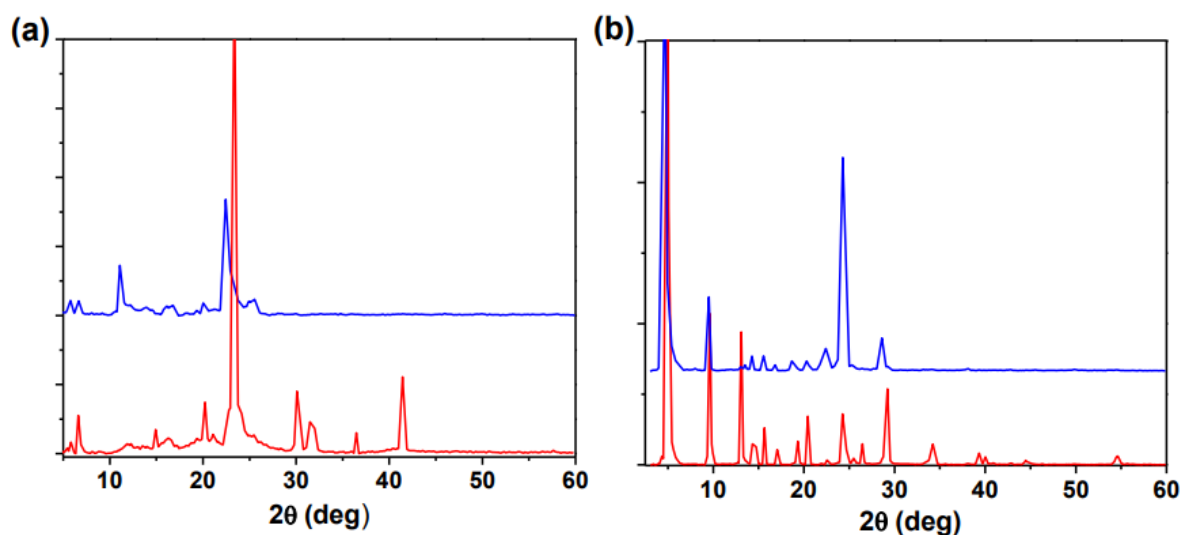


Fig. S9: Powder X-ray diffractograms of (a) **CSO** (**CSO1** (red curve) and **CSO2** (blue curve)) (b) **CSM** (**CSM1** (red curve) and **CSM2** (blue curve)).

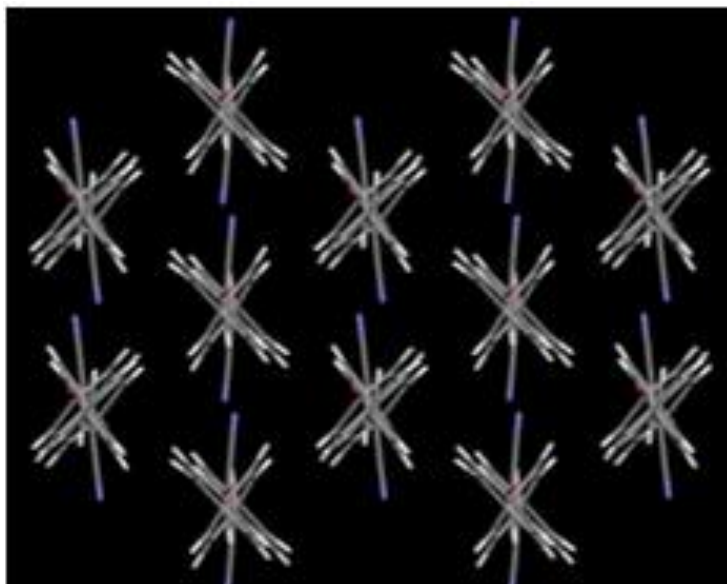


Fig. S10: Slipped molecular arrangement in the packing of **CSP1**. (Alkyl chains are removed for clarity)

References

1. S. J. Yoon, J. W. Chung, J. Gierschner, K. S. Kim, M. G. Choi, D. Kim and S. Y. Park, *J. Am. Chem. Soc.*, 2010, **132**, 13675.