

Aggregation Induced Emission by Pyridinium-Pyridinium Interactions

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General considerations

Column chromatography was performed using reversed phase C18-silica gel columns (RP18 25-40 μm) and direct phase silica gel columns.

Nuclear magnetic resonance spectra were recorded on NMR spectrometers at the following frequencies: ^1H , 400 MHz; $^{13}\text{C}\{^1\text{H}\}$, 100.6 MHz. Chemical shifts are reported in parts per million (ppm) relative to TMS or with the residual solvent peak as an internal reference. High-resolution mass spectra (HRMS) were recorded on a mass spectrometer with a time-of-flight (TOF) mass analyzer using the ESI technique. Melting points are uncorrected.

Unless otherwise noted, all chemicals were used as received from commercial sources. Anhydrous THF, diethyl ether and CH_2Cl_2 were obtained by passing commercially available solvents through activated alumina columns.

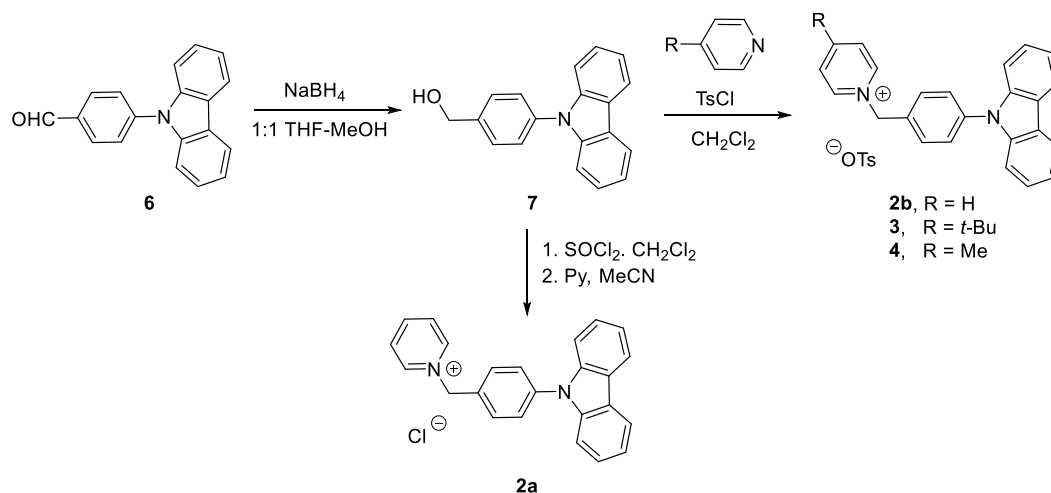
The luminescence data was collected with Edinburgh Instruments *FS5* Spectrofluorometer; photoluminescence quantum yields (PLQY) were measured using an integrating sphere.

Experimental procedures for synthesis of quaternary pyridinium salts 1–5

1-Benzylpyridin-1-ium bromide (1). Pyridine (0.32 mL, 4.00 mmol, 1.2 equiv) was added to a colorless solution of benzyl bromide (0.57 g, 3.34 mmol, 1.0 equiv) in anhydrous acetone (15 mL) in a 20 mL pressure vial. The vial sealed, stirred at 90 $^\circ\text{C}$ for 1h, cooled to ambient temperature and concentrated under reduced pressure. The resulting pale yellow oil was re-evaporated with anhydrous MeCN 10 times to give highly viscous oil. The oil was triturated with EtOAc to afford white crystalline material. The highly hygroscopic solid was filtered under Ar atmosphere to afford the desired product as a white crystalline solid (0.79 g, 3.15 mmol, 94%). ^1H NMR was consistent with that of previously reported product.¹

^1H -NMR (400 MHz, CDCl_3 , δ) 9.65–9.60 (m, 2H), 8.44–8.38 (m, 1H), 8.04–7.99 (m, 2H), 7.72–7.66 (m, 2H), 7.40–7.33 (m, 3H), 6.35 (s, 2H) ppm;

Synthesis of carbazoles 2–4



(4-(9*H*-Carbazol-9-yl)phenyl)methanol (7) was synthesized using a modified literature procedure.² Accordingly, finely ground NaBH₄ (0.14 g, 3.69 mmol, 2.0 equiv) was added to a cooled (0 °C) solution of aldehyde **6** (0.50 g, 1.84 mmol, 1.0 equiv) in a mixture of THF (15 mL) and MeOH (15 mL). The cloudy reaction mixture was stirred at 0 °C (crushed ice) for 1h, then warmed to room temperature, stirred for additional 16 h and diluted with water (100 mL) and aqueous 1M HCl (10 mL). The resulting solution was extracted with DCM (3x50 mL), combined organic extracts were dried over Na₂SO₄ and concentrated. The colorless glassy residue was dissolved in DCM (10 mL) under reflux, and hexane (20 mL) was added. The resulting solution was partially concentrated (to a half of the original volume) on a rotatory evaporator to remove most of the DCM, whereupon white solid precipitate was formed. More hexane (20 mL) was added and the resulting suspension was heated under reflux for 2-3 min, cooled to room temperature, sonified for 5 min in an ultrasound bath and left in freezer (-15 °C) for 1h. The white solid was cold-filtered, and the filter cake was washed with hexane to give the desired product **2** as a white solid (0.44 g, 1.60 mmol, 87%). ¹H NMR was consistent with previously reported product.³

¹H-NMR (400 MHz, CDCl₃, δ) 8.17–8.13 (m, 2H), 7.64–7.55 (m, 4H), 7.44–7.38 (m, 4H), 7.32–7.27 (m, 2H), 4.84 (s, 2H) ppm;

1-(4-(9*H*-Carbazol-9-yl)benzyl)pyridin-1-ium chloride (2a). To a solution of alcohol **7** (0.20 g, 0.73 mmol, 1.0 equiv) in anhydrous DCM (10 mL) was added SOCl₂ (0.21 mL, 2.93 mmol, 4.0 equiv). The resulting a clear pale yellow solution was stirred at room temperature for 30 min, then concentrated under reduced pressure and redissolved in MeCN (4.0 mL). Pyridine (0.15 mL, 1.83 mmol, 2.5 equiv) was

added, and the resulting clear solution was heated at 80 °C for 1 h. Evaporation and purification by reversed phase column chromatography using gradient elution from 10% acetonitrile in water to 100% acetonitrile afforded crude product **2a**. The obtained oily material was re-dissolved in MeCN (5 mL) and evaporated *in vacuo*. The dissolution/evaporation cycle was repeated 3 times, affording title product **2a** as a white solid (0.19 g, 0.51 mmol, 70%).

Mp 227.5-229.0 °C (Toluene/EtOH);

¹H-NMR (300 MHz, (CD₃)₂SO, δ): 9.42–9.34 (m, 2H), 8.73–8.65 (m, 1H), 8.30–8.22 (m, 4H), 7.90–7.82 (m, 2H), 7.78–7.71 (m, 2H), 7.48–7.36 (m, 4H), 7.34–7.26 (m, 2H), 6.06 (s, 2H) ppm;

¹³C NMR (133 MHz, (CD₃)₂SO, δ): 146.1, 145.0, 139.8, 137.8, 133.3, 130.8, 128.6, 127.3, 126.3, 122.8, 120.6, 120.3, 109.6, 62.7 ppm;

HRMS (*m/z*) Calc. Mass for C₂₄H₁₉N₂⁺: 335.1548; Found: 335.1547;

IR (KBr, cm⁻¹): 3434, 3043, 1455, 1232.

General procedure for synthesis of **2b**, **3** and **4**

To a colorless solution of alcohol **2** (1.00 mmol, 1.0 equiv) in CH₂Cl₂ (10 mL) was added TsCl (3.00 mmol, 3.0 equiv), followed by the corresponding pyridine (6.00 mmol, 6.0 equiv). The resulting colorless solution was stirred at room temperature for 24h, whereupon all volatiles were removed *in vacuo* and the colored oily residue was purified by reversed phase column chromatography using gradient elution from 10% acetonitrile in water to 100% acetonitrile to give pyridinium salts **2b**, **3** and **4**.

1-(4-(9H-Carbazol-9-yl)benzyl)pyridin-1-ium 4-methylbenzenesulfonate (2b) was synthesized according to the General Procedure. Crude material was recrystallized from CH₂Cl₂/Hexane to afford the title product as colorless crystals (0.29 g, 0.57 mmol, 57%).

Mp 212.0-213.6 °C (CH₂Cl₂/Hexane).

¹H-NMR (400 MHz, (CD₃)₂SO, δ) 9.34–9.30 (m, 2H), 8.71–8.65 (m, 1H), 8.27–8.22 (m, 4H), 7.86–7.82 (m, 2H), 7.76–7.71 (m, 2H), 7.52–7.47 (m, 2H), 7.46–7.36 (m, 4H), 7.33-7.27 (m, 2H), 7.12-7.08 (m, 2H), 6.02 (s, 2H), 2.27 (s, 3H) ppm;

^{13}C NMR (133 MHz, $(\text{CD}_3)_2\text{SO}$, δ): 146.5, 146.2, 145.4, 140.3, 138.2, 138.0, 133.7, 131.2, 129.0, 128.5, 127.7, 126.8, 125.9, 123.3, 121.0, 120.7, 110.0, 63.3, 21.2 ppm;

HRMS (m/z) Calc. Mass for $\text{C}_{24}\text{H}_{19}\text{N}_2^+$: 335.1548; Found: 335.1544

IR (KBr, cm^{-1}): 3420, 3059, 1450, 1210.

1-(4-(9H-Carbazol-9-yl)benzyl)-4-(tert-butyl)pyridin-1-ium 4-methylbenzene sulfonate (3) was synthesized according to the General Procedure. Crude material was recrystallized from EtOAc/MeCN to afford the title product as colorless crystals (0.36 g, 0.63 mmol, 63%).

Mp 190.0-191.5 °C (EtOAc/MeCN)

^1H -NMR (300 MHz, $(\text{CD}_3)_2\text{SO}$, δ) 9.23–9.18 (m, 2H), 8.29–8.22 (m, 4H), 7.87–7.81 (m, 2H), 7.77–7.72 (m, 2H), 7.50–7.36 (m, 6H), 7.34–7.27 (m, 2H), 7.13–7.08 (m, 2H), 5.95 (s, 2H), 2.28 (s, 3H), 1.38 (s, 9H) ppm;

^{13}C NMR (133 MHz, $(\text{CD}_3)_2\text{SO}$, δ): 170.5, 145.8, 144.3, 139.8, 137.7, 137.5, 133.4, 130.7, 128.0, 127.3, 126.3, 125.6, 125.5, 122.9, 120.6, 120.3, 109.6, 61.9, 36.4, 29.5, 20.8 ppm;

HRMS (m/z) Calc. Mass for $\text{C}_{28}\text{H}_{27}\text{N}_2^+$: 391.2174; Found: 391.2176;

IR (KBr, cm^{-1}): 3459, 3047, 2967, 1452, 1188.

1-(4-(9H-Carbazol-9-yl)benzyl)-4-methylpyridin-1-ium 4-methylbenzenesulfonate (4) was synthesized according to the General Procedure. Crude material was recrystallized from EtOAc/MeOH to afford the title product as colorless crystals (0.28 g, 0.53 mmol, 53%).

Mp 212.1-214.7 °C (EtOAc/MeOH);

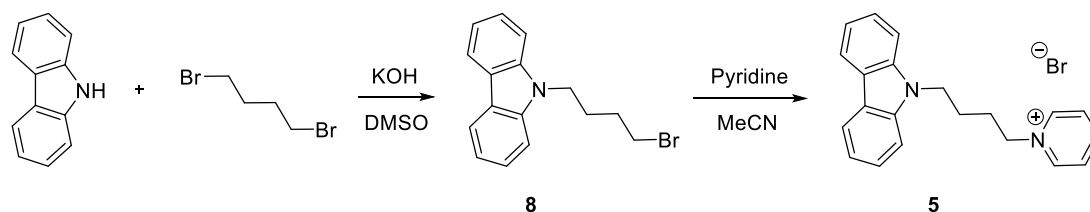
^1H -NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$, δ) 9.17–9.12 (m, 2H), 8.28–8.22 (m, 2H), 8.09–8.04 (m, 2H), 7.83–7.71 (m, 4H), 7.50–7.35 (m, 6H), 7.33–7.27 (m, 2H), 7.13–7.08 (m, 2H), 5.92 (s, 2H), 2.63 (s, 3H), 2.28 (s, 3H) ppm;

^{13}C NMR (133 MHz, $(\text{CD}_3)_2\text{SO}$, δ): 159.5, 145.9, 143.9, 139.8, 137.7, 137.4, 133.4, 130.5, 128.8, 128.0, 127.2, 126.3, 125.5, 122.8, 120.5, 120.2, 109.5, 62.0, 21.4, 20.7 ppm;

HRMS (m/z) Calc. Mass for $C_{25}H_{21}N_2^+$: 349.1705; Found: 349.1710;

IR (KBr, cm^{-1}): 3428, 3039, 1452, 1189.

Synthesis of carbazole **5**



9-(4-Bromobutyl)-9H-carbazole (8) was synthesized using a modified literature procedure.⁴ Accordingly, carbazole (0.84 g, 5.00 mmol, 1.0 equiv), KOH (0.55 g, 10.00 mmol, 2.0 equiv) and DMSO (8 mL) were combined in a 20 mL pressure vial. The initially formed suspension was stirred at room temperature until KOH was completely dissolved. Then 1,4-dibromobutane (1.18 mL, 10.00 mmol, 2.0 equiv) was added to the clear dark-colored DMSO solution and sonified in an ultrasound bath at room temperature. After sonication for 10 min, colorless solid precipitate started to form. After 30 min of sonication the resulting suspension was diluted with water (150 mL) and extracted with EtOAc (3x 100 mL). Combined organic extracts were dried over Na_2SO_4 , filtered and concentrated *in vacuo*. The oily residue was purified by column chromatography on silica gel using 4% of EtOAc in petroleum ether as a mobile phase. Crude product **8** was recrystallized from EtOH to afford the title compound as colorless crystals (0.72 g, 2.39 mmol, 48%). 1H NMR was consistent with that of the reported product.⁵

1H -NMR (400 MHz, $CDCl_3$, δ) 8.13–8.09 (m, 2H), 7.50–7.45 (m, 2H), 7.43–7.39 (m, 2H), 7.27–7.21 (m, 2H), 4.36 (t, $J = 6.9$ Hz, 2H), 3.38 (t, $J = 6.5$ Hz, 2H), 2.11–2.03 (m, 2H), 1.96–1.88 (m, 2H) ppm;

1-(4-(9H-Carbazol-9-yl)butyl)pyridin-1-ium bromide (5). To a solution of 4-bromobutyl carbazole **8** (0.20 g, 0.66 mmol, 1.0 equiv) in acetonitrile (3 mL) in a 5 mL pressure vial was added pyridine (0.11 mL, 1.32 mmol, 2.0 equiv). The vial was sealed and heated at 90 °C for 16 h whereupon all volatiles were removed *in vacuo* and the residue was dissolved in DCM (1 mL). To the DCM solution was added hexane (20 mL). Formed precipitate was filtered to afford the title product as colorless solid (0.18 g, 0.46 mmol, 69%).

Mp 175.0-175.8 °C (EtOAc/MeCN)

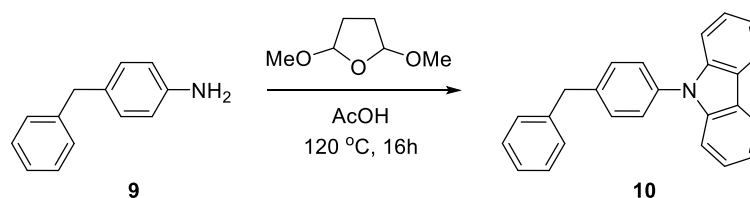
¹H-NMR (300 MHz, CDCl₃, δ): 9.04–8.98 (m, 2H), 8.21–8.13 (m, 1H), 8.09-8.04 (m, 2H), 7.75-7.67 (m, 2H), 7.49-7.38 (m, 4H), 7.26–7.19 (m, 2H), 4.77–4.68 (m, 2H), 4.45–4.35 (m, 2H), 2.09–1.93 (m, 4H) ppm;

¹³C NMR (133 MHz, CDCl₃, δ): 144.8, 144.7, 140.1, 128.0, 126.2, 122.8, 120.5, 119.3, 109.1, 61.0, 42.3, 29.5, 25.1 ppm;

HRMS (*m/z*) Calc. Mass for C₂₁H₂₁N₂⁺: 301.1705; Found: 301.1714;

IR (KBr, cm⁻¹): 3456, 3050, 2942, 1632, 1489.

Synthesis of 9-(4-benzylphenyl)-9*H*-carbazole (**10**)



9-(4-Benzylphenyl)-9*H*-carbazole (10**)** was synthesized using a modified literature procedure.⁶ Accordingly, 2,5-dimethoxytetrahydrofuran (3.53 mL, 27.29 mmol, 4.0 equiv) was added to a clear brown solution of 4-benzylaniline (**9**, 1.25g, 6.82 mmol, 1.0 equiv) in glacial acetic acid (30 mL) in a 100 mL pressure vial. The vial was sealed and heated at 120 °C. The solution turned black during the first several minutes of the heating. After 16h the reaction mixture was cooled to ambient temperature, diluted with CH₂Cl₂ (150 mL) and water (150 mL) and slowly neutralized by addition of solid K₂CO₃ (*Caution! Intense gas evolution!*). Additional CH₂Cl₂ (50 mL) and water (150 mL) was added after the gas evolution was ceased. Phases were separated, and aqueous phase was washed with CH₂Cl₂ (3x50 mL). Combined organic phases were dried over Na₂SO₄, concentrated *in vacuo* and filtered through a silica plug (150 mL of silica gel) using 15:1 hexane:EtOAc as a mobile phase. The filtrate was concentrated *in vacuo* and the white solid residue was further purified by reversed-phase column chromatography. Recrystallization of the desired product from acetone/MeOH afforded **10** as colorless needles (0.39 g, 1.18 mmol, 17%).

Mp 112.8-113.4 °C (Acetone/MeOH);

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ) 8.14 (dd, $J = 7.8, 1.0$ Hz, 1H), 8.13 (dd, $J = 7.8, 1.0$ Hz, 1H), 7.49–7.45 (m, 2H), 7.43–7.34 (m, 8H), 7.31–7.24 (m, 5H), 4.11 (s, 2H) ppm;

$^{13}\text{C NMR}$ (133 MHz, CDCl_3 , δ): 141.1, 140.8, 140.7, 135.8, 130.4, 129.2, 128.8, 127.3, 126.5, 126.0, 123.4, 120.4, 119.9, 110.0, 41.8 ppm;

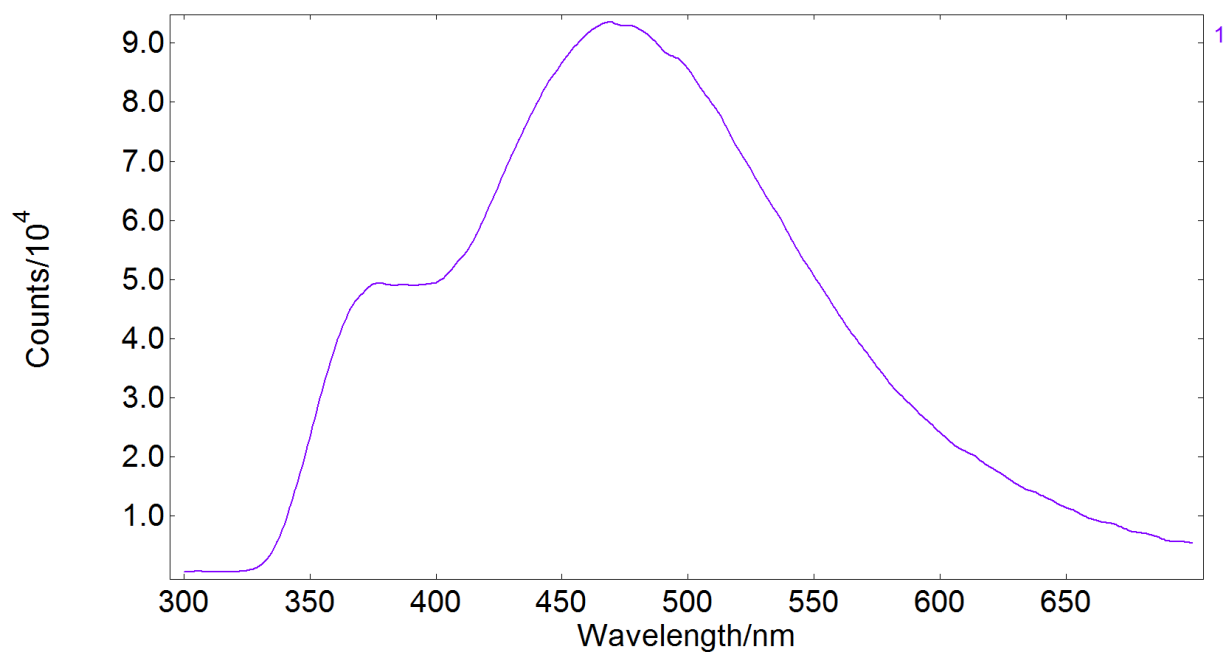
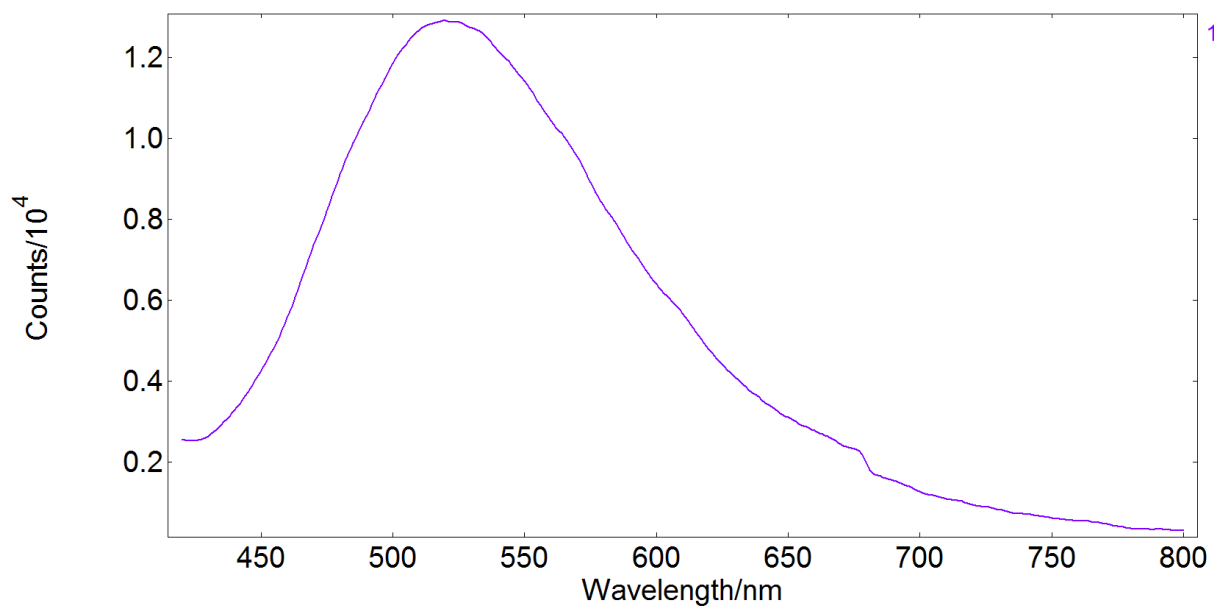
HRMS (m/z) Calc. Mass for $\text{C}_{25}\text{H}_{20}\text{N}^+$: 334.1596; Found: 334.1595;

Calculated for: $\text{C}_{25}\text{H}_{19}\text{N}$: C, 90.06; H, 5.74; N, 4.20. Found: C, 89.95; H, 5.70; N, 4.17;

IR (KBr, cm^{-1}): 3060, 3026, 2915, 1514, 1452, 1230

References

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6. Lee, D.H.; Lee, S.G.; Jung, D.I.; Hahn, J.T. *Asian J. Chem.* **2013**, *25*, 501-504.

Photophysical properties of pyridinium salt 1**Fig. S1.** Emission of **1** in MeCN solution (at 10^{-6} mol/L)**Fig. S2.** The solid-state emission of **1** (excited at 393 nm)

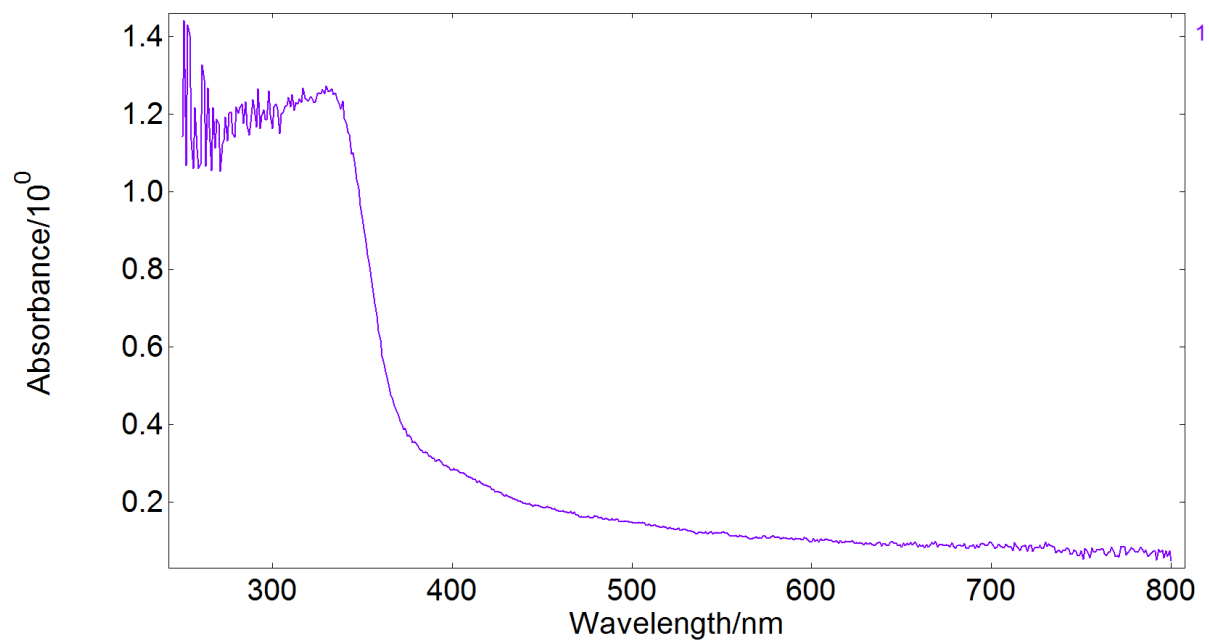


Fig. S3. Absorbance of **1** in the solid-state.

Absorbance of 2-5 in the solid state

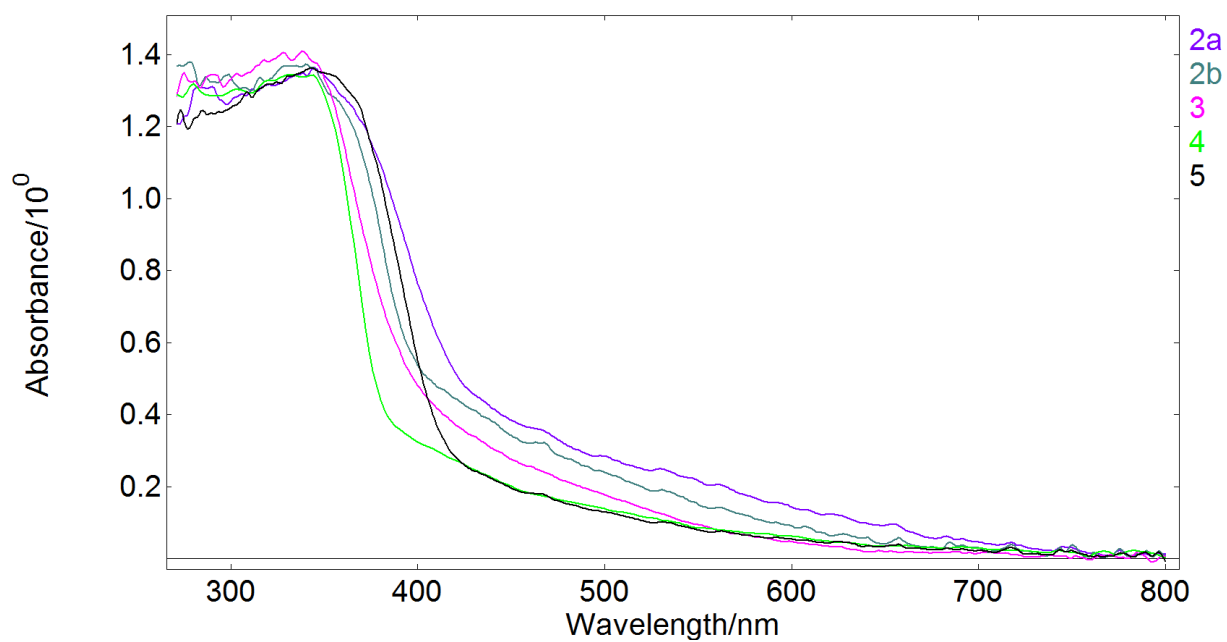
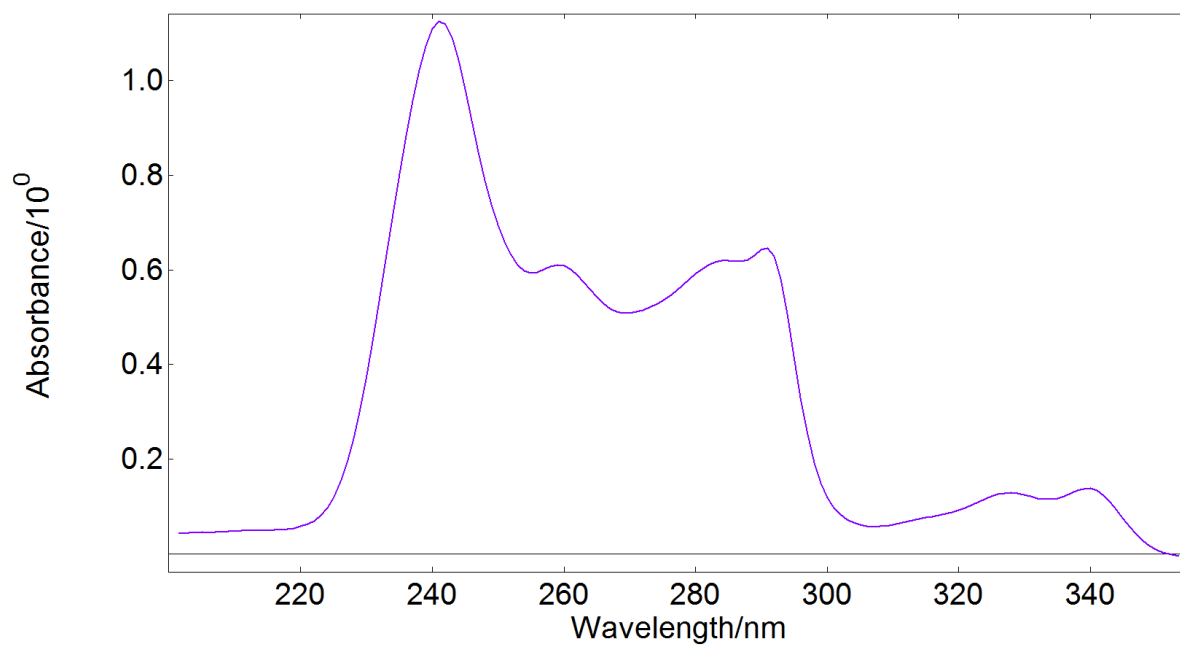
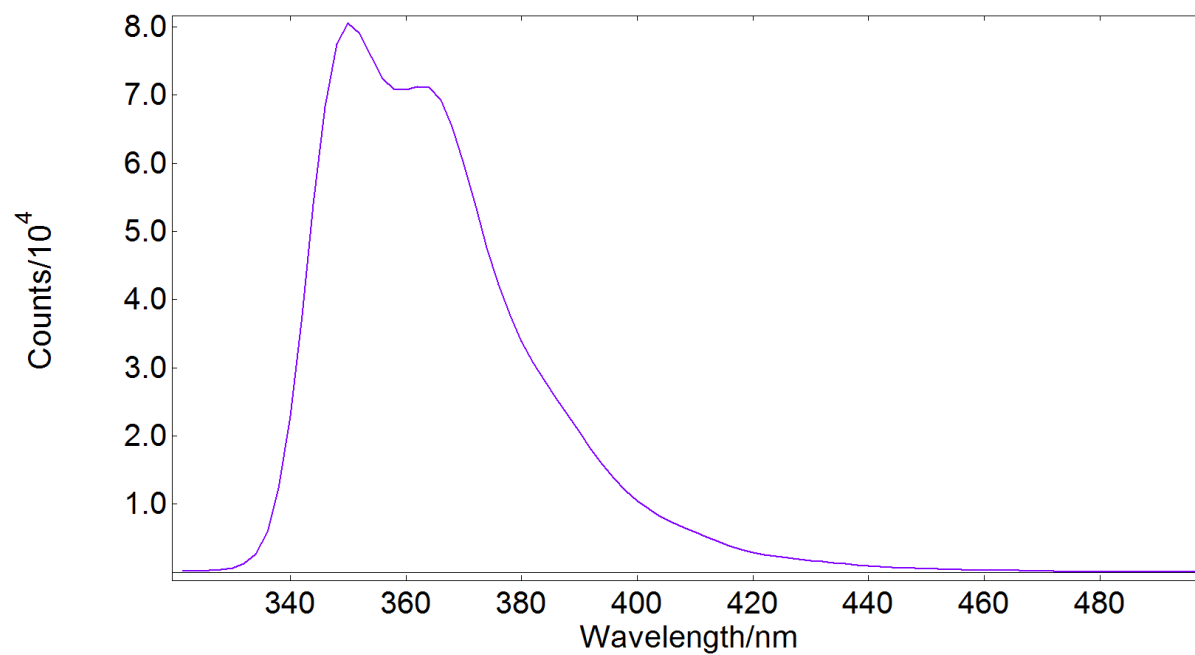


Fig. S4. Absorbance of **2–5** in the solid-state.

Photophysical properties of phenyl carbazole 10

Entry	λ_{Abs} , nm	MeCN λ_{Em} , nm	solid λ_{Em} , nm	solution ϕ (%)	solid ϕ (%)	α_{AIE}
1	240, 259, 291, 329	349, 364	414, 435, 463	39.9	35.5	0.89

**Fig. S5.** Absorption of **10** in MeCN solution (at 10^{-6} mol/L)**Fig. S6.** Emission of **10** in MeCN solution (at 10^{-6} mol/L)

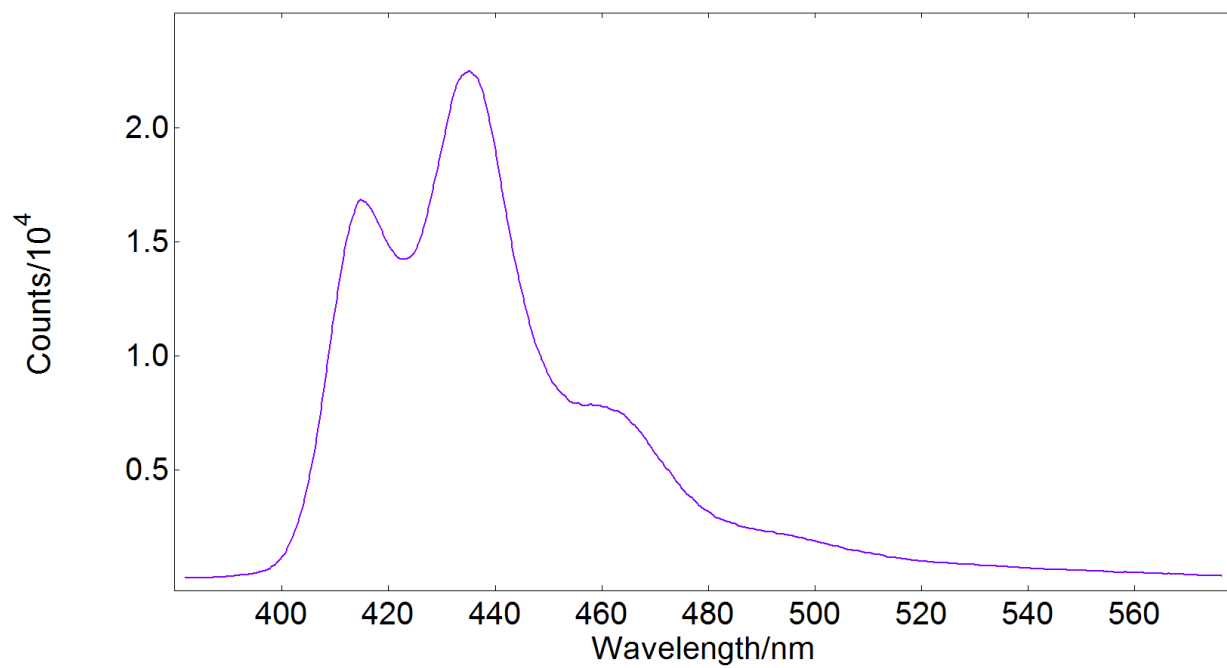


Fig. S7. The solid-state emission of **10**

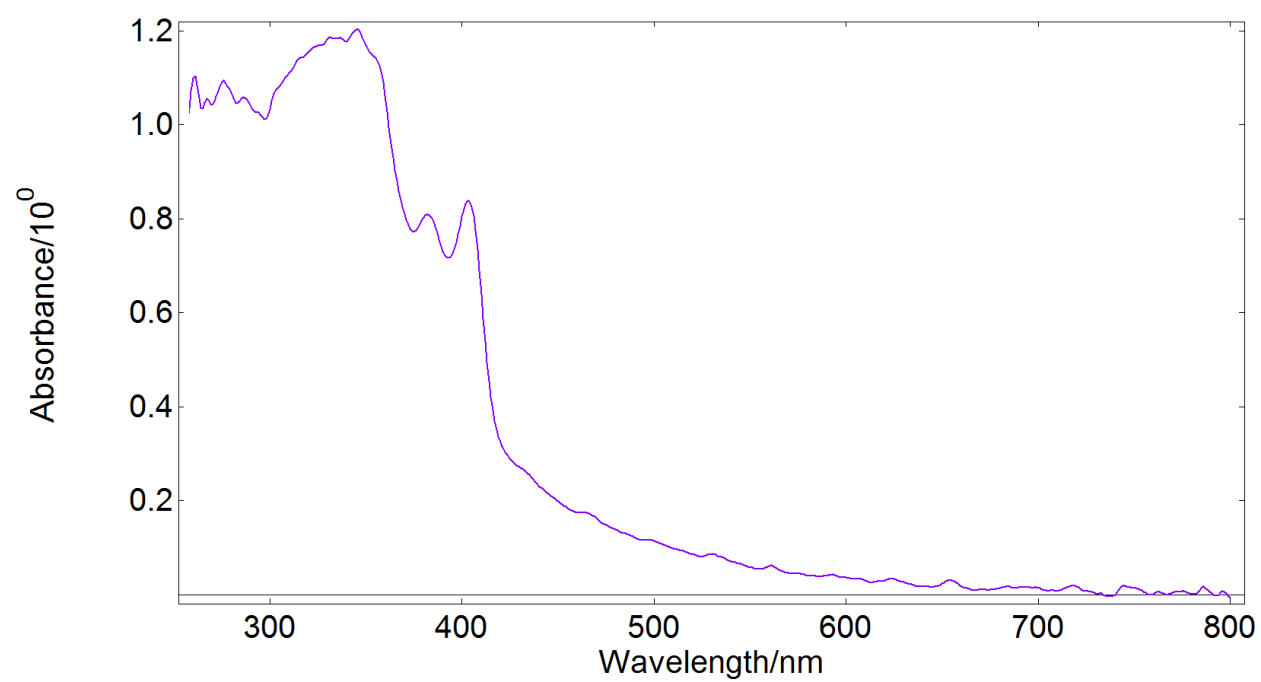


Fig. S8. The solid-state absorbance of **10**

Photoluminescence behaviour of **2a** in various solvent mixtures

Since **2a** is salt, the addition of water (a poor solvent) to a solution of **2a** in organic solvent (good solvent) cannot be used. Instead, acetonitrile and diethyl ether were chosen as the good and the poor solvents, respectively. No substantial emission of **2a** could be observed upon addition of Et₂O (up to 80% v/v) to a solution of **2a** in MeCN. However, when the proportion of Et₂O in the mixture of solvents reached 90-95% (v/v), a strong emission had become visible (Fig. S9). The emission spectra for the most non-polar solvent mixture (95% Et₂O in MeCN) was distorted due to the formation of larger particles that move within the cuvette.

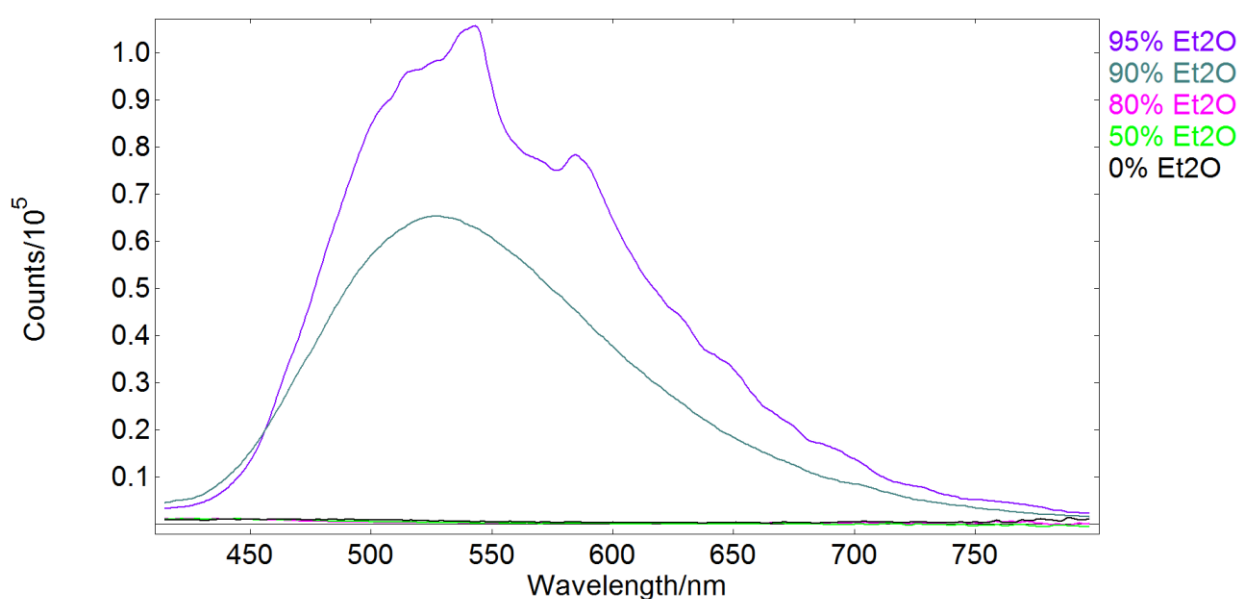


Fig. S9. Photoluminescence spectra of **2a** in MeCN/Et₂O solvent mixtures

Dynamic light scattering measurements for **2a**.

Dynamic light scattering (DLS) measurements for **2a** were carried out using *Malvern Zetasizer ZSP* with *Malvern Instruments Ltd* software 7.11. The presence of aggregates was determined in the centre of a glass cuvette at 20°C and at backscatter angle of 173° with laser attenuator set to 11. Refractive index of acetonitrile and diethyl ether mixtures was calculated using Lorentz-Lorentz equation (1):

$$\frac{n^2 - 1}{n^2 + 2} = \left(\frac{n_1^2 - 1}{n_1^2 + 2} \right) \phi_1 + \left(\frac{n_2^2 - 1}{n_2^2 + 2} \right) \phi_2 \quad (1)$$

where, n is the refractive index of the mixture of x_1 and x_2 , n_1 and n_2 are the refractive indices of the pure components respectively, ϕ_1 and ϕ_2 are volume fractions.

Viscosity of the solvent mixtures was calculated using equation 2:

$$\eta = \eta_1^x \times \eta_2^{1-x} \quad (2)$$

where η_1 and η_2 are viscosities of individual solvents and x – molar fractions of components of the binary system.

Concentration of the samples were 0.02 mg/mL. Fig. S10 represents the DLS measurement scattered light intensity graphically.

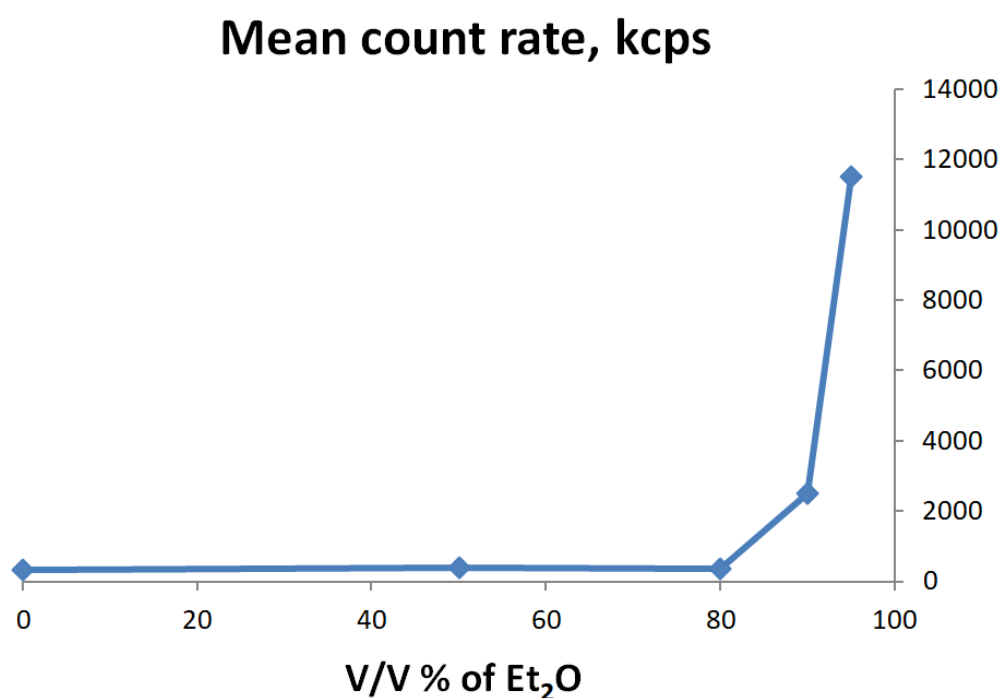
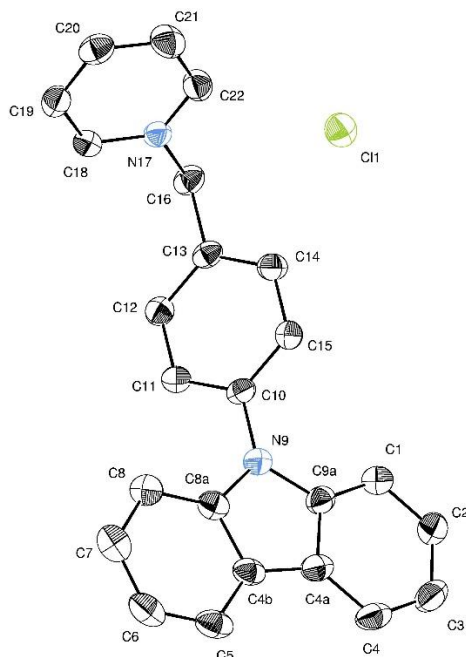


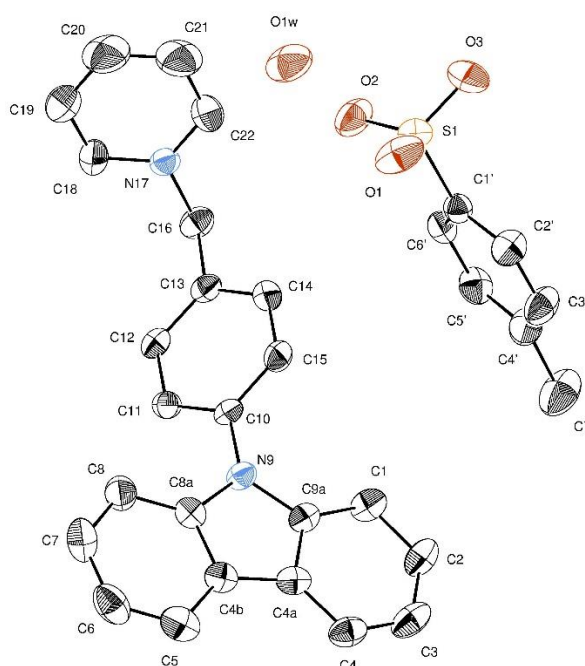
Fig. S10. Scattering values observed in MeCN/Et₂O mixtures of **2a**.

Conclusions from the experiments:

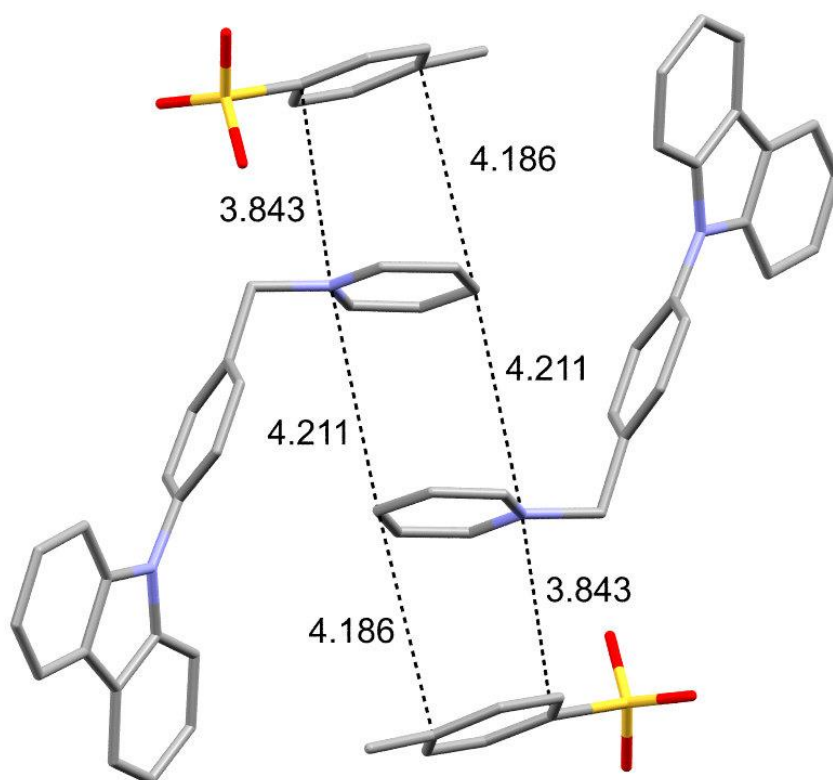
1. No aggregates or nano-aggregates were observed until 80% v/v of Et₂O in MeCN as evidenced by the constant scattering value observed in the samples;
2. Aggregates could be observed at 90-95% v/v of Et₂O in MeCN, as indicated by the rapid increase in the scattering value;
3. Aggregates observed at 90-95% v/v of Et₂O in MeCN were plainly visible with the naked eye and their size exceeded that of the DLS measurement capacity (particle size was above 10 μm).

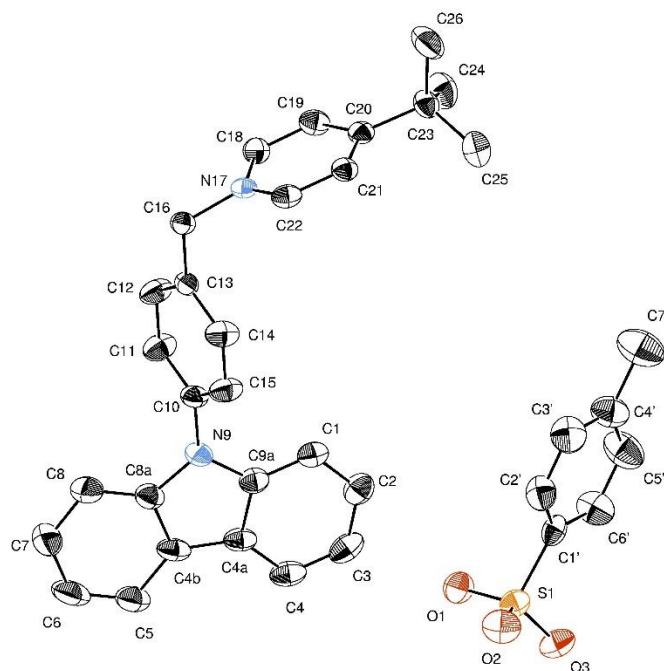
X-Ray Structure, crystal data and structure refinements for 2a

Identification code	kl_1143_3
Empirical formula	C ₂₄ H ₁₉ Cl N ₂
Formula weight	370.86
Temperature	190(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P c a b
Unit cell dimensions	a = 8.2062(2) Å alpha = 90 deg.
	b = 18.5089(6) Å beta = 90 deg.
	c = 24.6576(8) Å gamma = 90 deg.
Volume	3745.19(19) Å ³
Z, Calculated density	8, 1.315 Mg/m ³
Absorption coefficient	0.215 mm ⁻¹
F(000)	1552
Crystal size	0.31 x 0.12 x 0.10 mm
Two-theta max. for data	55.0 deg.
Limiting indices	-10 ≤ h ≤ 10, -23 ≤ k ≤ 24, -31 ≤ l ≤ 32
Reflections collected / unique	7963 / 4274 [R(int) = 0.1037]
Completeness to theta = 25.242	99.30%
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4274 / 0 / 244
Goodness-of-fit on F ²	0.953
Final R indices [I > 2σ(I)]	R1 = 0.0610, wR2 = 0.1111
R indices (all data)	R1 = 0.1556, wR2 = 0.1384
Extinction coefficient	0
Largest diff. peak and hole	0.226 and -0.263 e.Å ⁻³

X-Ray Structure, crystal data and structure refinements for 2b

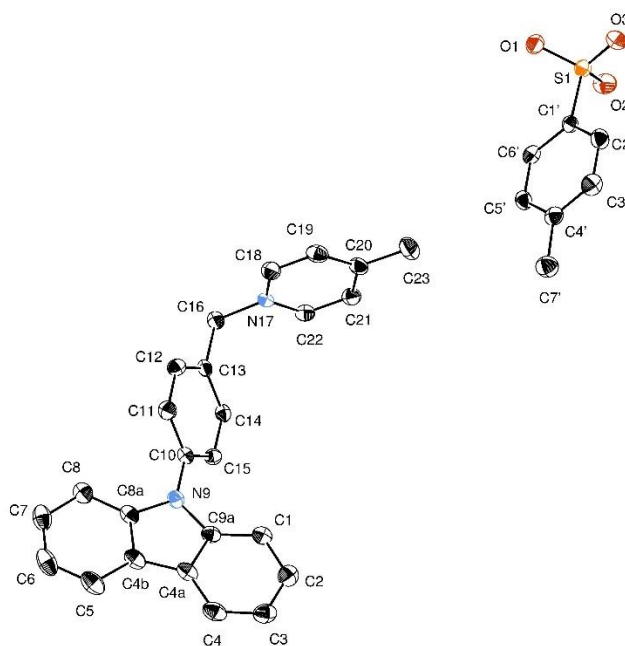
Identification code	Substance_2b
Empirical formula	C ₆₂ H ₅₄ N ₄ O ₇ S ₂
Formula weight	1031.21
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P 2 ₁ /n
Unit cell dimensions	a = 16.19500(59) Å alpha = 90.0000 deg. b = 9.75520(29) Å beta = 101.7706(15) deg. c = 16.75330(80) Å gamma = 90.0000 deg.
Volume	2591.122(176) Å ³
Z, Calculated density	2, 1.322 Mg/m ³
Absorption coefficient	0.163 mm ⁻¹
F(000)	1084
Crystal size	0.19 x 0.18 x 0.10 mm
Two-theta max. for data	56.0 deg.
Limiting indices	-21 ≤ h ≤ 21, -12 ≤ k ≤ 12, -22 ≤ l ≤ 21
Reflections collected / unique	11181 / 6155 [R(int) = 0.1123]
Completeness to theta = 28.0	99.50%
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6155 / 2 / 350
Goodness-of-fit on F ²	0.998
Final R indices [I > 2σ(I)]	R ₁ = 0.0734, wR ₂ = 0.1328
R indices (all data)	R ₁ = 0.1966, wR ₂ = 0.1700
Largest diff. peak and hole	0.425 and -0.335 e.Å ⁻³

Expanded view of pyridinium cation-tosylate anion interactions for 2b

X-Ray Structure, crystal data and structure refinements for 3

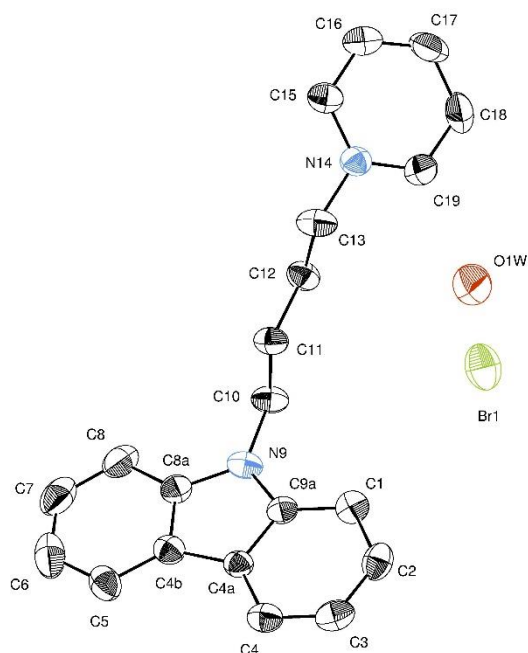
Identification code	734new_i2a_ns_sq
Empirical formula	C ₃₅ H ₃₄ N ₂ O ₃ S
Formula weight	562.7
Temperature	190(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, I 2/a
Unit cell dimensions	a = 29.4101(10) Å alpha = 90 deg. b = 8.4373(2) Å beta = 115.777(2) deg. c = 30.7626(11) Å gamma = 90 deg.
Volume	6873.9(4) Å ³
Z, Calculated density	8, 1.087 Mg/m ³
Absorption coefficient	0.127 mm ⁻¹
F(000)	2384
Crystal size	0.20 x 0.18 x 0.10 mm
Two-theta max. for data	55.0 deg.
Limiting indices	-38 ≤ h ≤ 38, -9 ≤ k ≤ 10, -39 ≤ l ≤ 39
Reflections collected / unique	11412 / 7378 [R(int) = 0.0798]
Completeness to theta = 25.242	94.40%
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	7378 / 0 / 374
Goodness-of-fit on F ²	0.986
Final R indices [I > 2σ(I)]	R1 = 0.0738, wR2 = 0.1717
R indices (all data)	R1 = 0.1680, wR2 = 0.2083
Extinction coefficient	0
Largest diff. peak and hole	0.397 and -0.404 e.Å ⁻³

X-Ray Structure, crystal data and structure refinements for 4



Identification code	lk_731b
Empirical formula	C ₃₂ H ₂₈ N ₂ O ₃ S
Formula weight	520.62
Temperature	190(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P c
Unit cell dimensions	a = 9.6828(2) Å alpha = 90 deg. b = 11.6284(3) Å beta = 100.0377(8) deg. c = 11.7511(3) Å gamma = 90 deg.
Volume	1302.87(5) Å ³
Z, Calculated density	2, 1.327 Mg/m ³
Absorption coefficient	0.162 mm ⁻¹
F(000)	548
Crystal size	0.24 x 0.15 x 0.10 mm
Two-theta max. for data	55.0 deg.
Limiting indices	-12 ≤ h ≤ 12, -13 ≤ k ≤ 15, -15 ≤ l ≤ 15
Reflections collected / unique	5423 / 5422 [R(int) = 0.0133]
Completeness to theta = 25.242	99.80%
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5422 / 2 / 346
Goodness-of-fit on F ²	1.017
Final R indices [I > 2σ(I)]	R1 = 0.0393, wR2 = 0.0840
R indices (all data)	R1 = 0.0500, wR2 = 0.0903
Absolute structure parameter	0.38(8)
Extinction coefficient	0
Largest diff. peak and hole	0.202 and -0.293 e.Å ⁻³

X-Ray Structure, crystal data and structure refinements for 5



Identification code	new
Empirical formula	C ₂₁ H ₂₁ Br N ₂ O
Formula weight	397.31
Temperature	190(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P b c a
Unit cell dimensions	a = 15.3118(3) Å alpha = 90 deg. b = 9.8222(2) Å beta = 90 deg. c = 26.0811(6) Å gamma = 90 deg.
Volume	3922.48(14) Å ³
Z, Calculated density	8, 1.346 Mg/m ³
Absorption coefficient	2.106 mm ⁻¹
F(000)	1632
Crystal size	0.14 x 0.10 x 0.06 mm
Two-theta max. for data	55.0 deg.
Limiting indices	-19 ≤ h ≤ 19, -12 ≤ k ≤ 12, -33 ≤ l ≤ 33
Reflections collected / unique	8360 / 4484 [R(int) = 0.0830]
Completeness to theta = 25.242	99.70%
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4484 / 0 / 226
Goodness-of-fit on F ²	1.03
Final R indices [I > 2σ(I)]	R ₁ = 0.0834, wR ₂ = 0.2285
R indices (all data)	R ₁ = 0.1688, wR ₂ = 0.2786
Extinction coefficient	0
Largest diff. peak and hole	1.816 and -1.122 e.Å ⁻³

Spectral data

