Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Substitution Pattern Controlled Aggregation-induced Emission in Donor-Acceptor-Donor Dyes with One and Two Propeller-like Triphenylamine Donors

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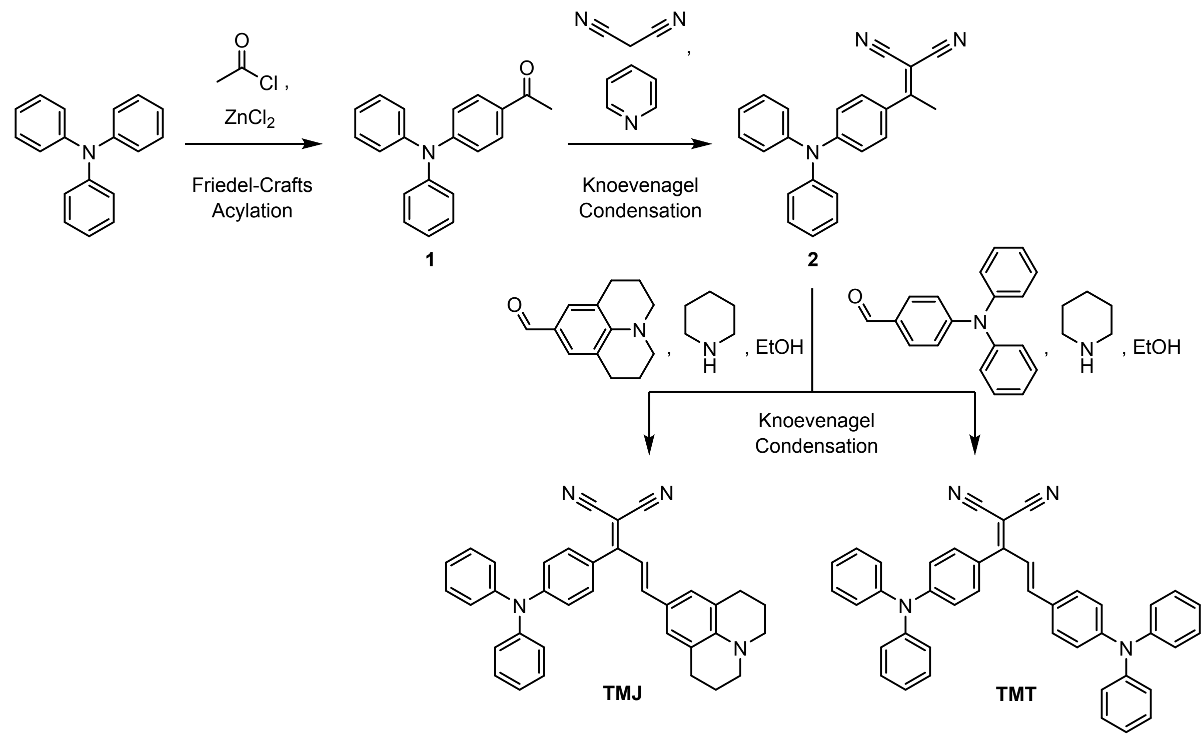
I Synthetic procedures

General

The syntheses of compounds **1**,[S1] **2**,[S2] **TMJ**,[S3] and **TMT**[S3] were adapted from literature procedures. Please note here, that we were not able to obtain the Knoevenagel product **2** by using the common catalyst system of ammonium acetate and acetic acid.



Scheme 1. Synthetic route to the D-A-D dyes TMJ and TMT.

Chemicals used for the synthesis. All anhydrous solvents were obtained from Sigma Aldrich and used as received. Triphenylamine and 4-(diphenylamino)benzaldehyde were purchased from chemPUR and malononitrile and julolidine-9-carbaldehyde were obtained from abcr GmbH. Anhydrous $ZnCl_2$, acetyl chloride, and piperidine were purchased from Sigma Aldrich.

Analytical characterization. NMR spectra were recorded on a JOEL ECP500 or BRUKER Avance 500 spectrometer. The peak assignment was carried out with the help of predicted spectra and multiplet analyses. Mass spectra were recorded on an Agilent 6210 TOF LC/MS System.

Synthesis

1-(4-(Diphenylamino)phenyl)ethanone (1). In a two-necked flask (50 mL) equipped with a septum and a condenser capped with a $CaCl_2$ drying tube triphenylamine (1.0 g, 4.08 mmol) and anhydrous $ZnCl_2$ (0.665 g, 4.88 mmol) were suspended in anhydrous dichloromethane (20 mL). After 10 min of stirring, acetyl chloride (290 µL, 0.320 g, 4.08 mmol) dissolved in anhydrous dichloromethane (5 mL) was added dropwise to the yellow-greenish suspension with a syringe under vigorous stirring over a period of 5 min. Subsequently, the resulting dark green mixture was refluxed for 20 h. After cooling, the mixture was poured into a cold HCl solution (1 M, 60 mL) and vigorously stirred for 5 min. Thereby, the initially dark green solution turned to yellow. The organic phase was separated in a separation funnel and the aqueous phase was extracted three times with CH_2Cl_2. The combined organic phases were then washed with saturated $NaHCO_3$ solution and brine and dried over $MgSO_4$. Subsequently, the solvent was removed under reduced pressure. The yellow residue was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate (9:1) as eluent. This yielded a white-yellow solid (0.79 g, 67 % yield, R_f = 0.43). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, J = 9.0 Hz, 2H), 7.34 – 7.28 (m, 4H), 7.17 – 7.11 (m, 6H), 6.98 (d, J = 8.9 Hz, 2H), 2.52 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 196.64, 152.31, 146.63, 130.02, 129.92, 129.74, 126.09, 124.77, 119.80, 26.36. MS (ESI-TOF): *m/z* $[M+Na]^+$ calcd for $C_{20}H_{17}NNaO$ 310.1202, found 310.1204.

2-(1-(4-(Diphenylamino)phenyl)ethylidene)malononitrile (2). Compound **1** (300 mg, 1.04 mmol) was dissolved in anhydrous pyridine (16 mL) and activated molecular sieve (0.5 g) and malononitrile (687 mg, 10.4 mmol) were added. The reaction mixture was stirred over night at 80 °C (17 h). After cooling, the mixture was diluted with dichloromethane (30 mL) and the molecular sieve was filtered off. Afterwards the organic layer was washed with water and brine. After drying over anhydrous $MgSO_4$, the solvent was removed by rotary evaporation. The dark red-brown residue was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate (9:1) as eluent. This yielded an orange solid (301 mg, 86 % yield, R_f = 0.39). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (d, J = 8.9 Hz, 2H), 7.37 – 7.32 (m, 4H), 7.21 – 7.15 (m, 6H), 6.98 (d, J = 8.9 Hz, 2H), 2.59 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.85, 152.12, 145.97, 129.92, 129.66, 126.80, 126.44, 125.45, 119.17, 114.38, 114.11, 79.94, 23.49. MS (ESI-TOF): *m/z* $[M+Na]^+$ calcd for $C_{23}H_{17}N_3Na$ 358.1315, found 358.1303.

(*E*)-2-(1-(4-(Diphenylamino)phenyl)-3-(9-julolidinyl)allylidene)malononitrile (TMJ). Julolidine-9-carbaldehyde (180 mg, 0.89 mmol) and compound **2** (300 mg, 0.89 mmol) were dissolved in anhydrous ethanol (20 mL). Piperidine was added in a catalytic amount (50 µL) and the reaction mixture was refluxed for 6 h. After cooling, the solvent was removed by rotary evaporation. The dark red residue was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate (9:1) as eluent, which yielded a red solid (297 mg, 64 % yield, R_f = 0.20). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 (t, J = 7.4 Hz, 4H), 7.26 (d, J = 15.1 Hz, 1H), 7.22 – 7.17 (m, 6H), 7.13 (t, J = 7.4 Hz, 2H), 7.05 (d, J = 8.8 Hz, 2H), 7.03 (s, 2H), 6.86 (d, J = 15.1 Hz, 1H), 3.29 (t, J = 5.8 Hz, 4H), 2.73 (t, J = 6.3 Hz, 4H), 1.96 (quint, J = 6.2 Hz, 4H). MS (ESI-TOF): *m/z* $[M+H]^+$ calcd for $C_{36}H_{31}N_4$ 519.2543, found 519.2559.

(*E*)-2-(1,3-bis(4-(diphenylamino)phenyl)allylidene)malononitrile (TMT). 4-(Diphenylamino)-benzaldehyde (244 mg, 0.89 mmol) and compound **2** (300 mg, 0.89 mmol) were dissolved in anhydrous ethanol (20 mL). Piperidine was added in a catalytic amount (50 µL) and the reaction mixture was refluxed for 6 h. After cooling, the solvent was removed by rotary evaporation. The dark orange residue was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate (9:1) as eluent, which yielded a orange solid (280 mg, 53 % yield, R_f = 0.51). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 – 7.34 (m, 4H), 7.34 – 7.29 (m, 7H), 7.25 (d, J = 8.7 Hz, 2H), 7.20 (d, J = 7.5 Hz, 4H), 7.16 – 7.12 (m, 8H), 7.06 (d, J = 8.6 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 15.3 Hz, 1H). MS (ESI-TOF): *m/z* $[M+Na]^+$ calcd for $C_{42}H_{30}N_4Na$ 613.2363, found 613.2379.

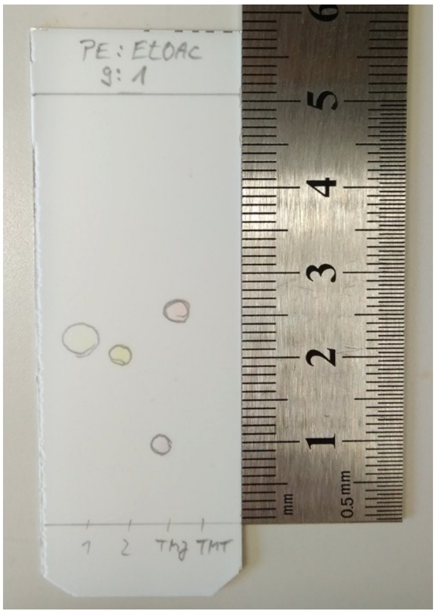


Figure S1. Thin layer chromatogram of compounds **1**, **2**, **TMJ**, and **TMT** using petroleum ether/ethyl acetate (9:1) as eluent.

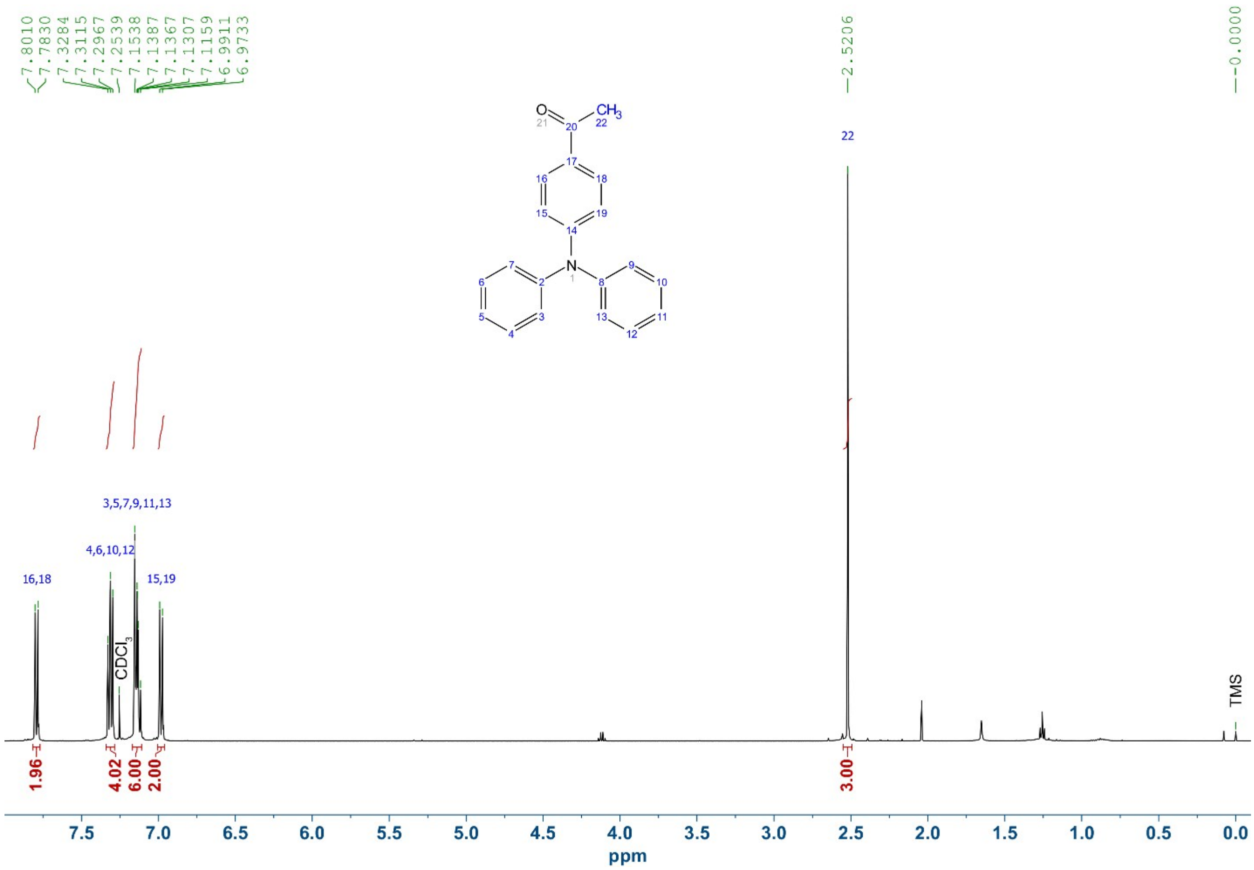


Figure S2. ^{1}H NMR of compound **1**.

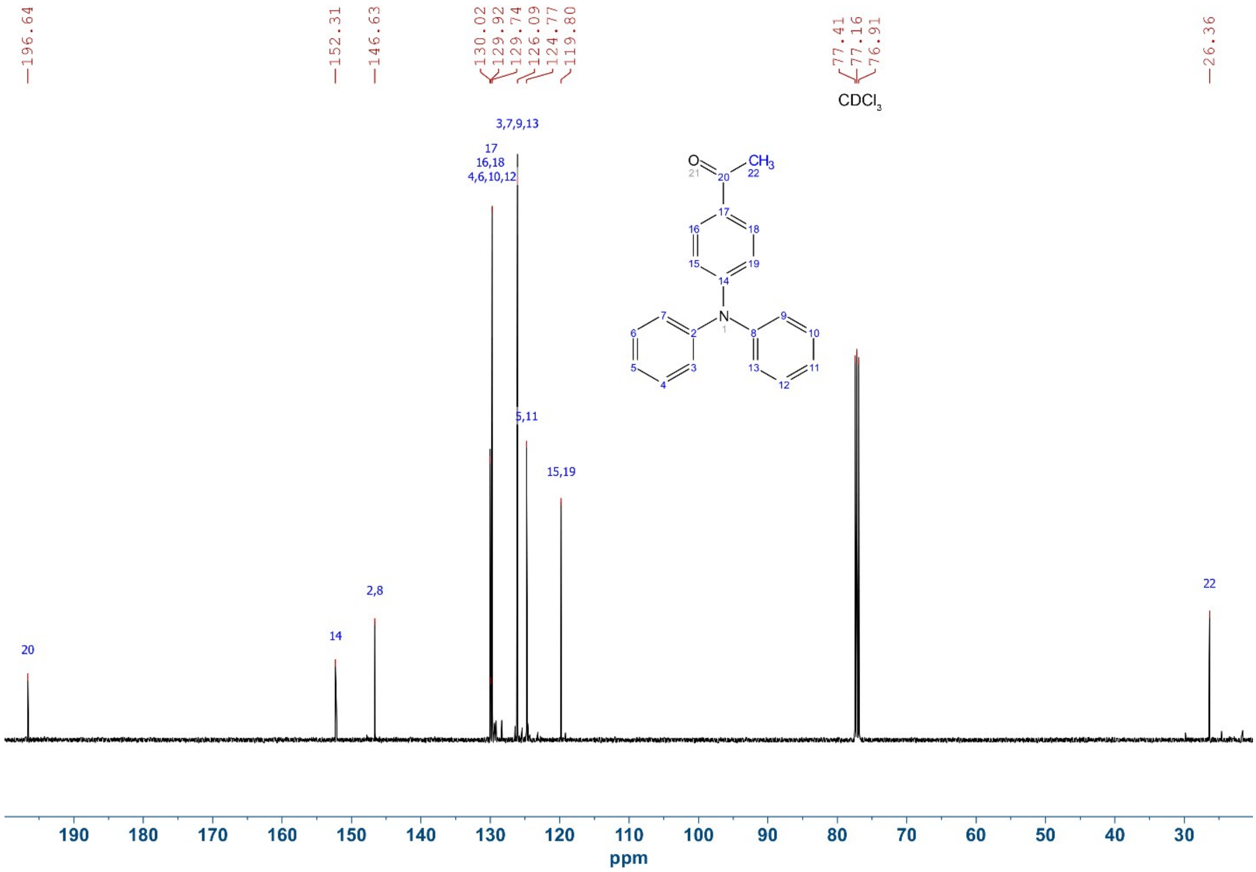


Figure S3. ^{13}C NMR of compound **1**.

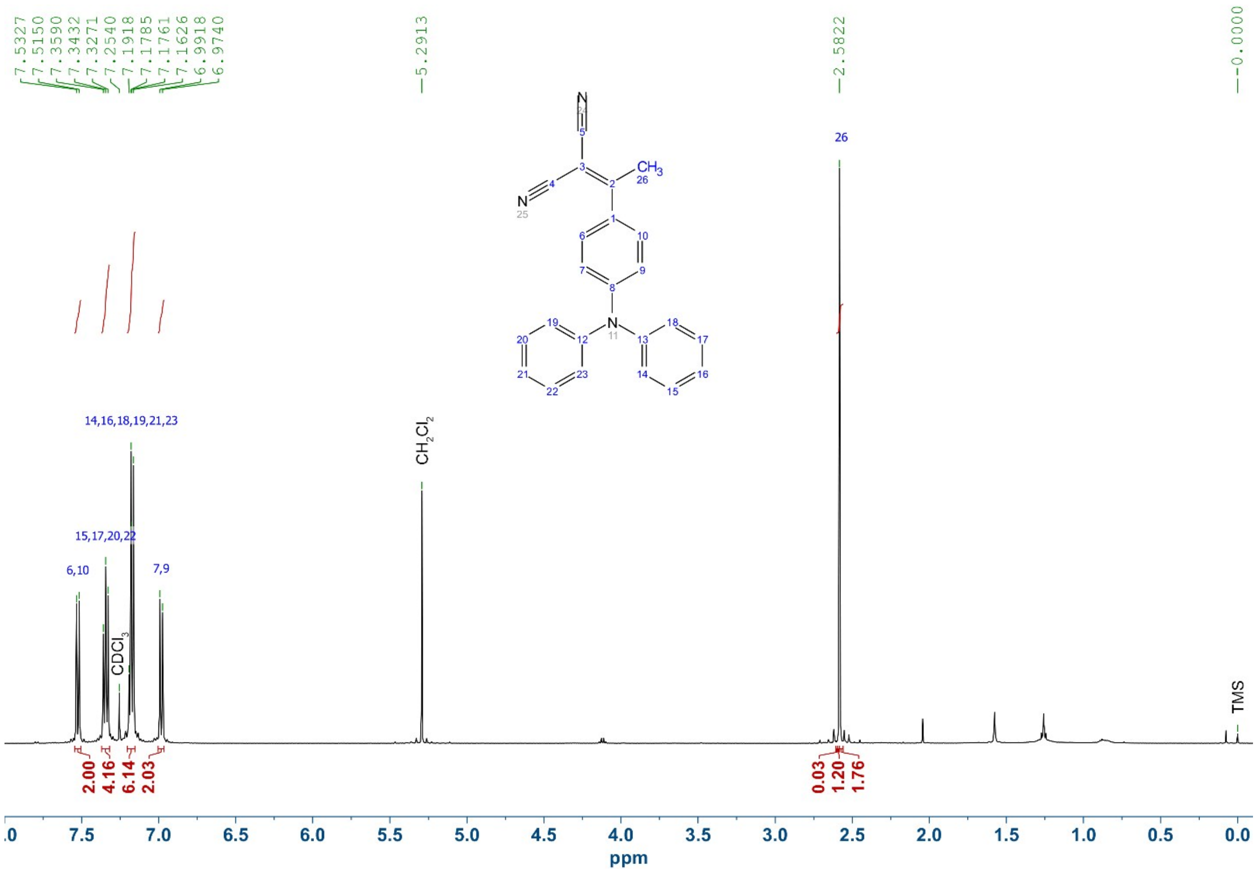


Figure S4. ^{1}H NMR of compound **2**.

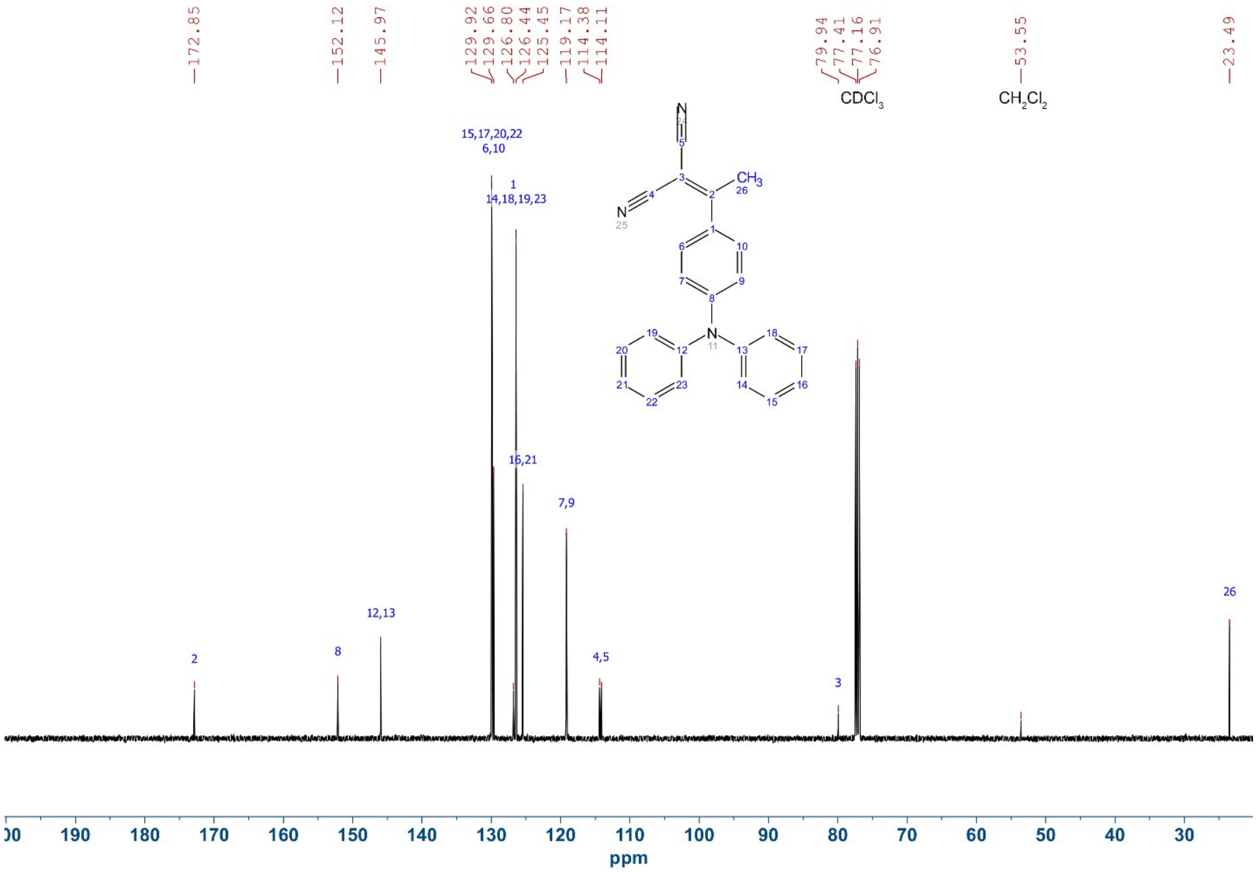


Figure S5. ^{13}C NMR of compound **2**.

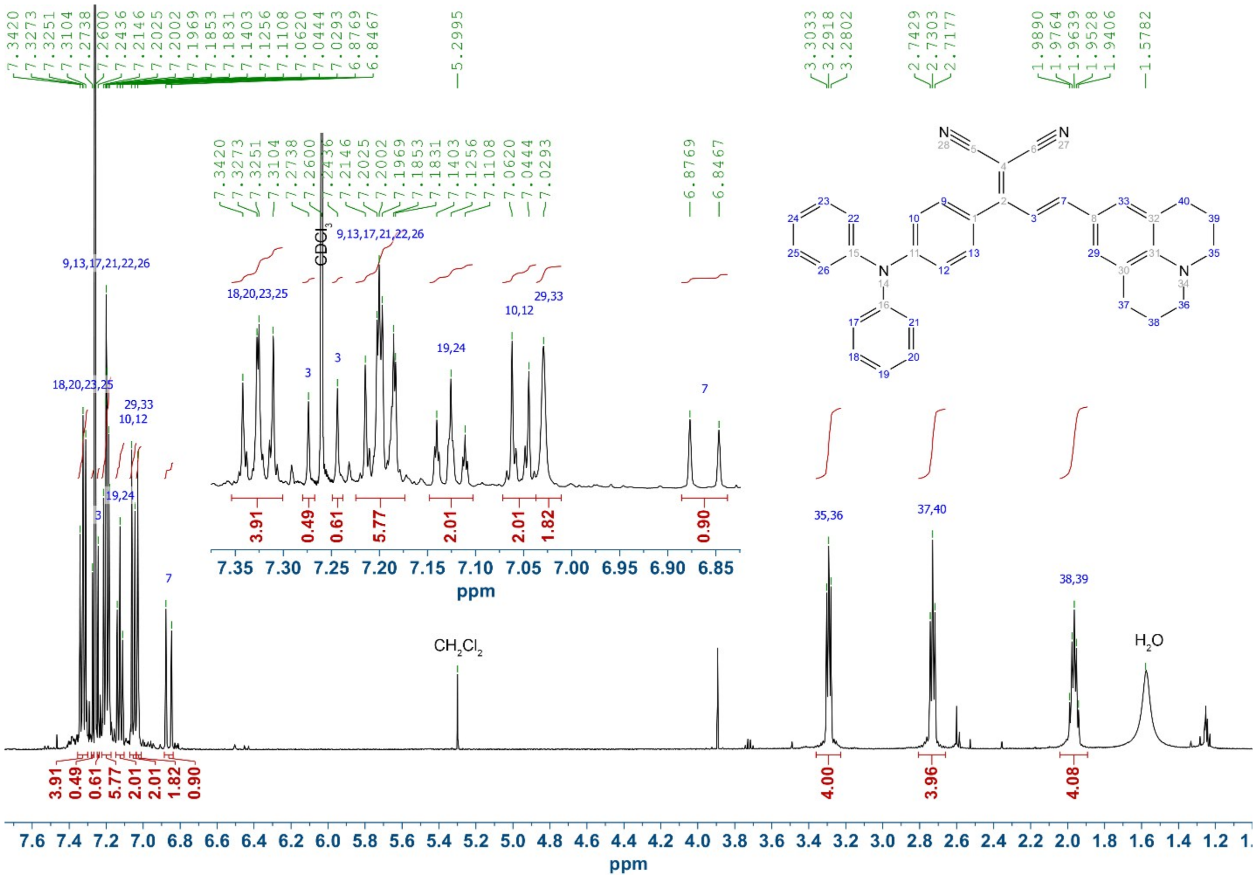


Figure S6. ^{1}H NMR of compound **TMJ**.

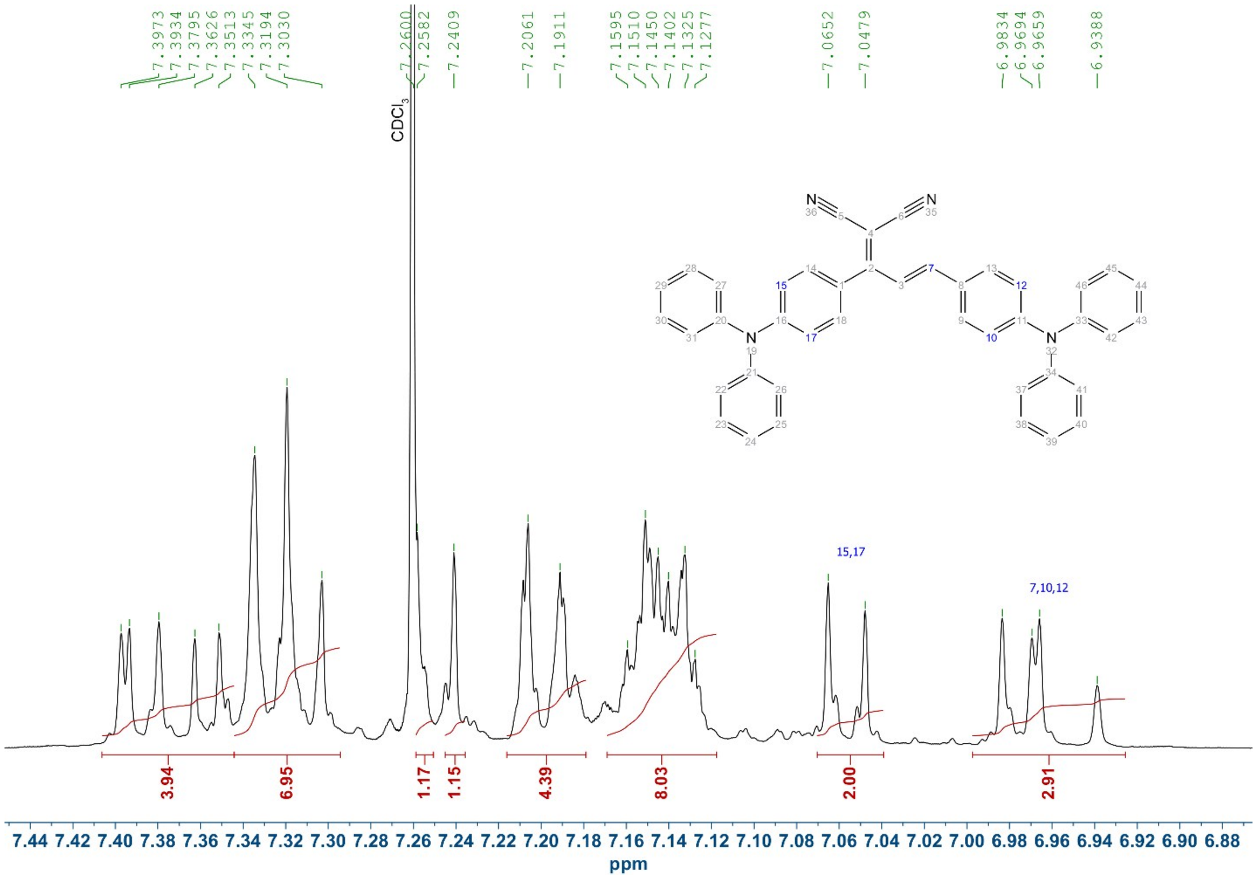


Figure S7. ^{1}H NMR of compound **TMT**.

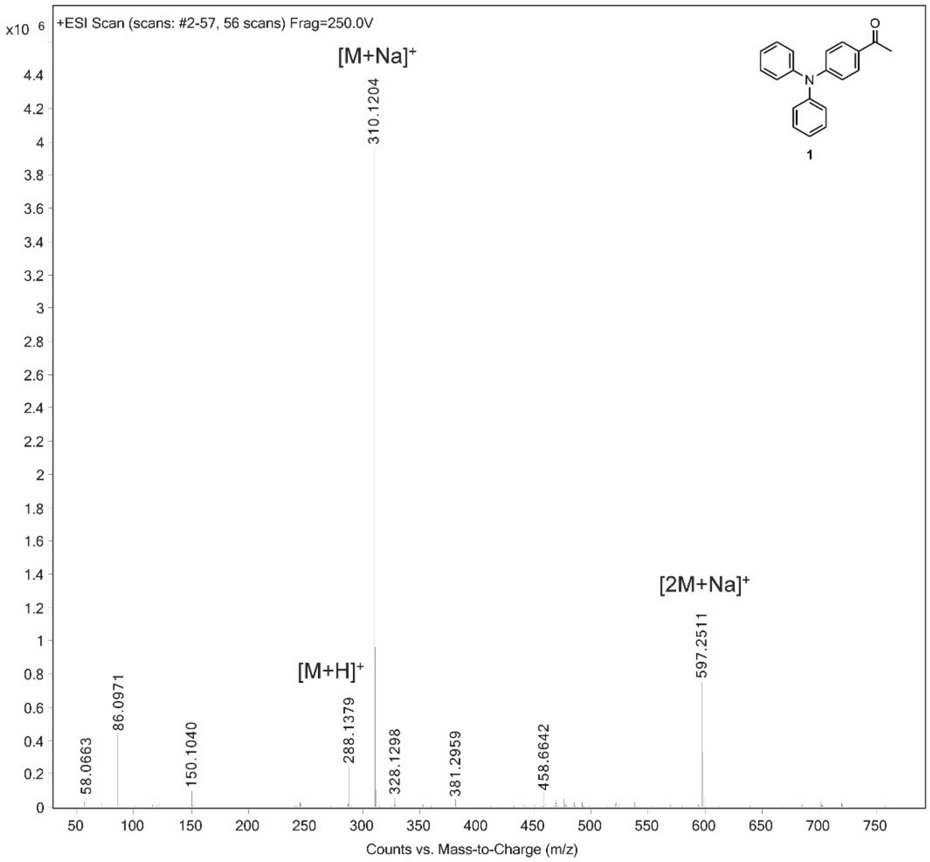


Figure S8. ESI-MS of compound **1**.

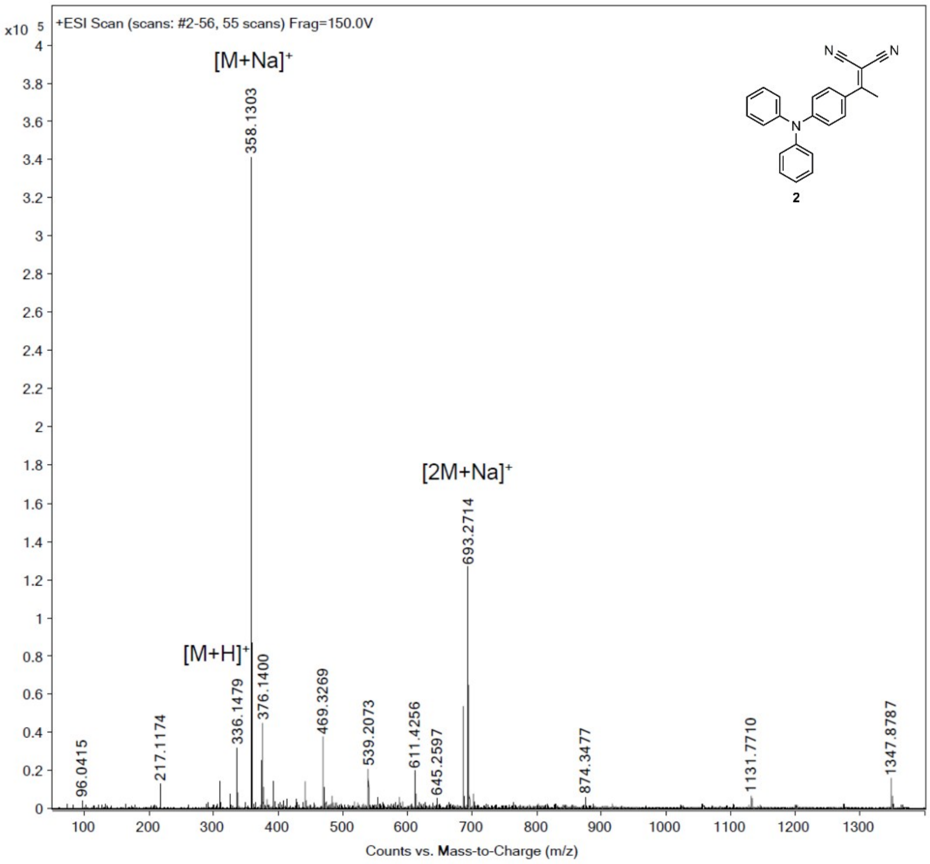


Figure S9. ESI-MS of compound **2**.

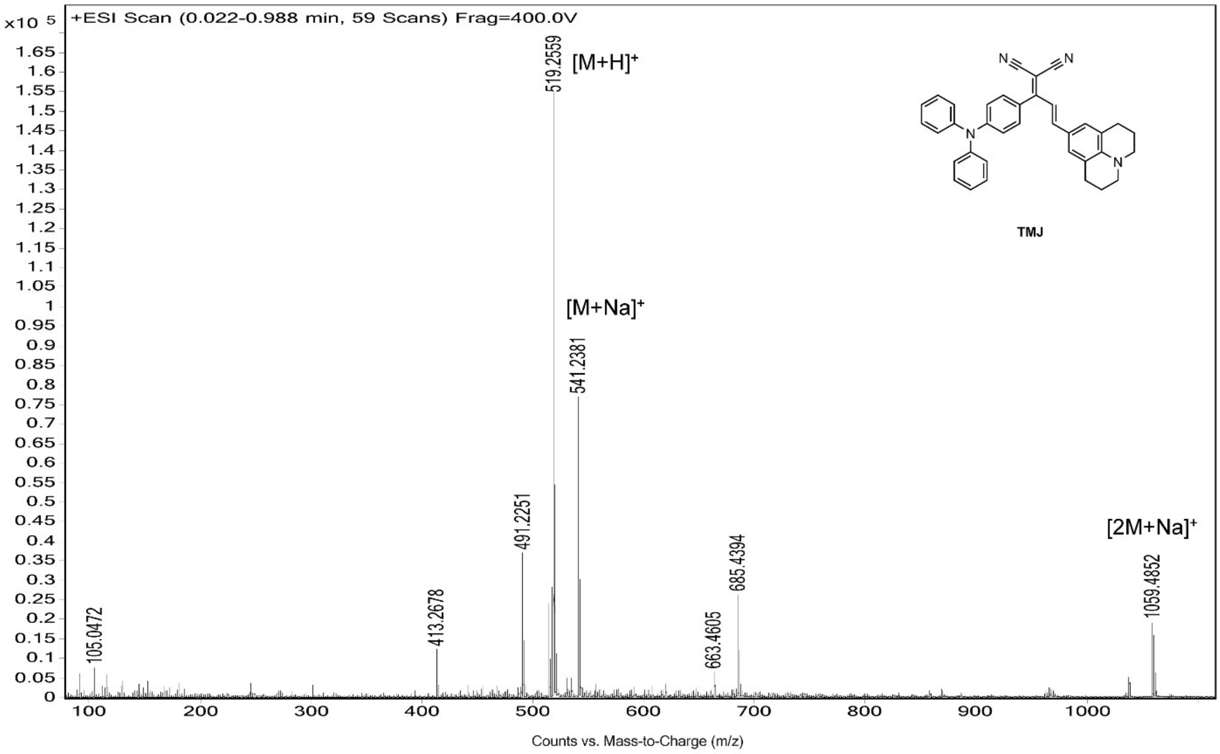


Figure S10. ESI-MS of **TMJ**.

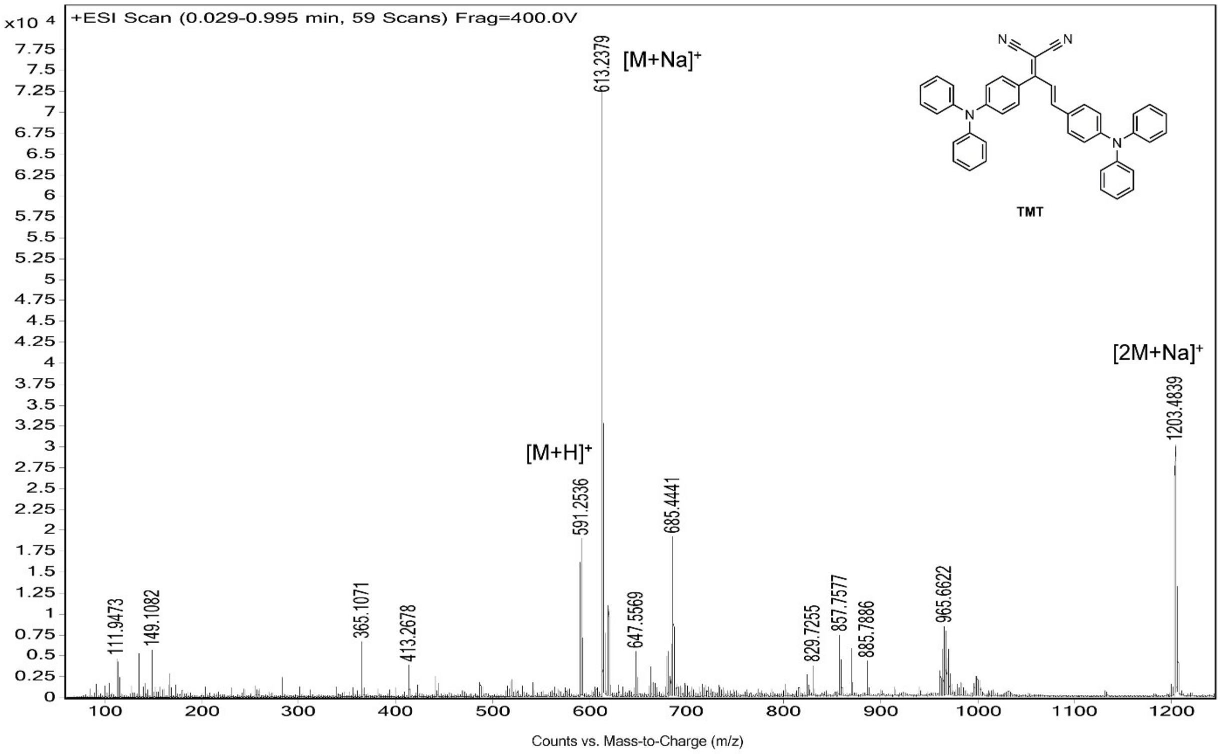


Figure S11. ESI-MS of **TMT**.

II Viscosity studies of TMT in acetonitrile (ACN)-PEG400 and toluene-paraffin (PAR) mixtures

Table S1. Measured densities ρ and dynamic viscosities η of the ACN-PEG and toluene- PAR mixtures.

ACN/PEG [v/v]	ρ (20 °C) [g·mL^{-1}]	η (20 °C) [mPa·s]	Tol/PAR [v/v]	ρ (20 °C) [g·mL^{-1}]	η (20 °C) [mPa·s]
100/0	0.7843	0.3720	100/0	0.8680	0.6161
70/30	0.8868	1.1713	70/30	0.8688	1.2724
50/50	0.9710	4.1152	50/50	0.8716	2.4434
40/60	0.9959	6.1500	40/60	0.8725	3.2108
30/70	1.0366	14.4762	30/70	0.8739	5.4431
20/80	1.0538	21.7972	20/80	0.8753	10.4245
10/90	1.0966	54.3671	10/90	0.8774	35.5198
5/95	1.1121	79.1037	5/95	0.8788	97.8069
2/98	1.1153	99.9220	2/98	0.8791	151.0539
0/100	1.1183	118.3805	0/100	0.8795	207.7694

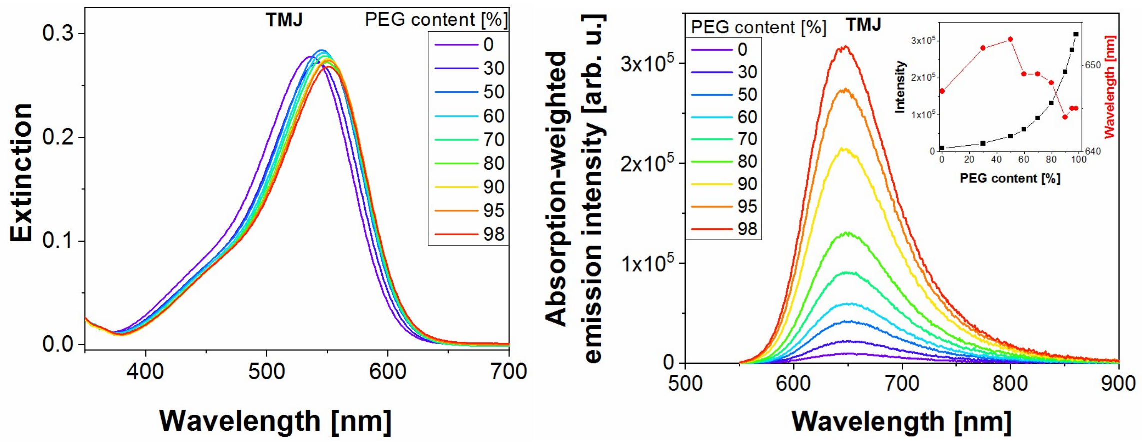


Figure S12. Absorption and absorption-weighted emission spectra (λ_{exc} = 536 nm) of TMJ (c = 7.5 μM) in ACN-PEG mixtures with increasing PEG content.

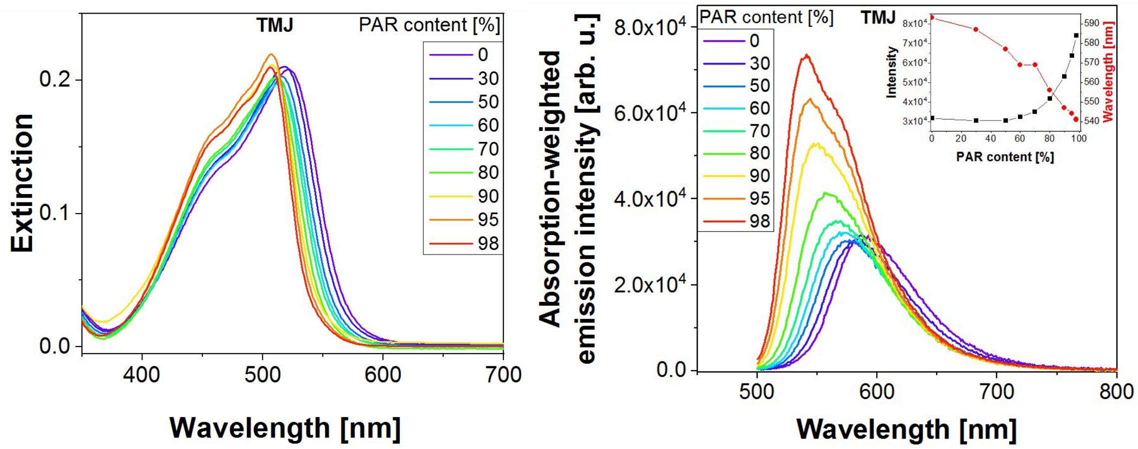


Figure S13. Absorption and absorption-weighted emission spectra (λ_{exc} = 521 nm) of TMJ (c = 7.5 µM) in toluene-PAR mixtures with increasing PAR content.

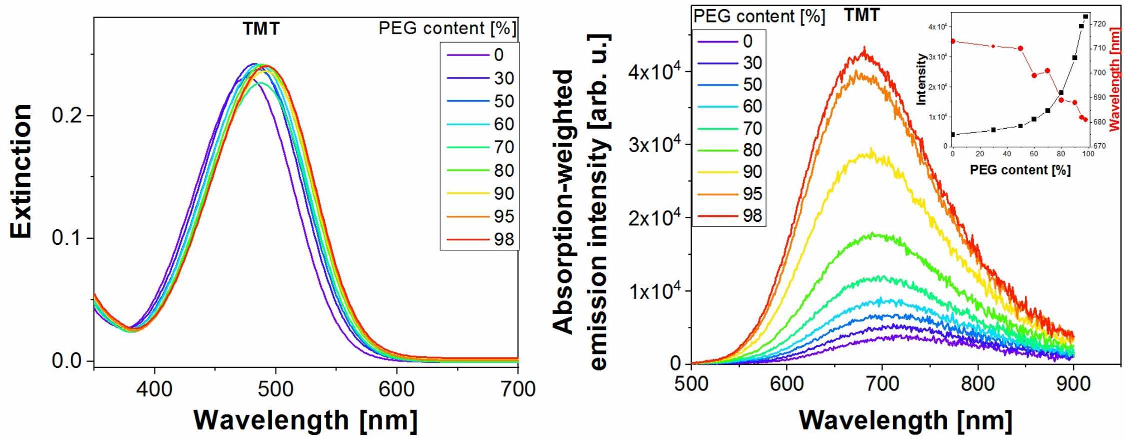


Figure S14. Absorption and absorption-weighted emission spectra (λ_{exc} = 476 nm) of TMT (c = 7.5 µM) in ACN-PEG mixtures with increasing PEG content.

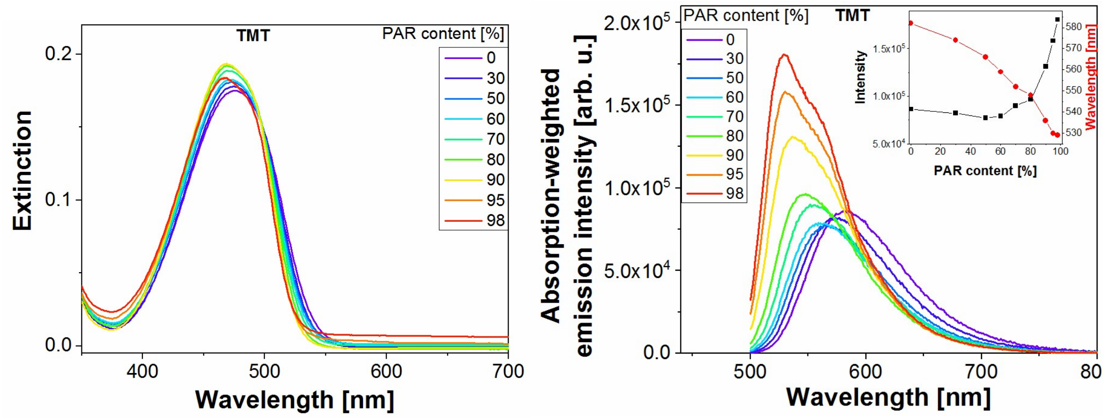


Figure S15. Absorption and absorption-weighted emission spectra (λ_{exc} = 476 nm) of TMT (c = 7.5 µM) in toluene-PAR mixtures with increasing PAR content.

III AIE studies of TMT and TMJ in ACN-water and dioxane-water mixtures

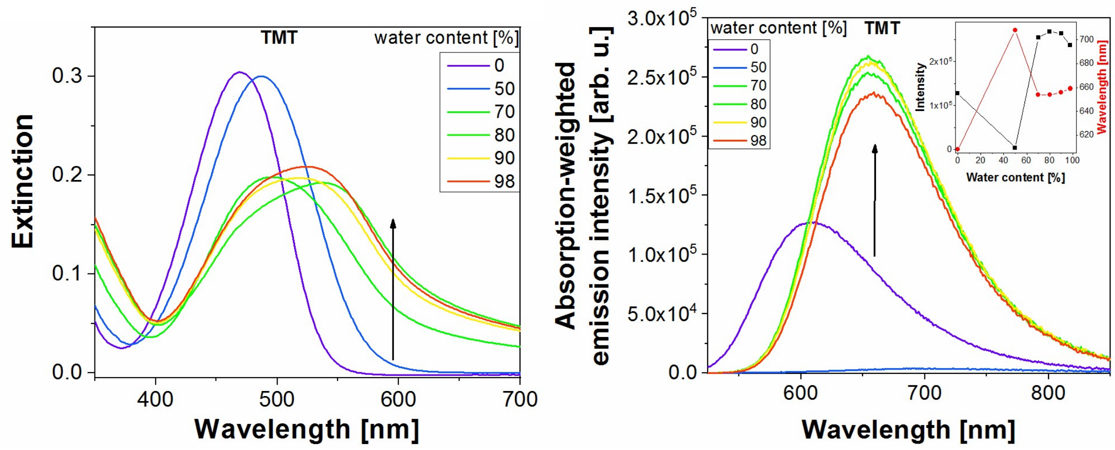


Figure S16. Absorption and absorption-weighted emission spectra (λ_{ex} = 469 nm) of TMT (c = 7.5 µM) in dioxane-water mixtures with increasing water content.

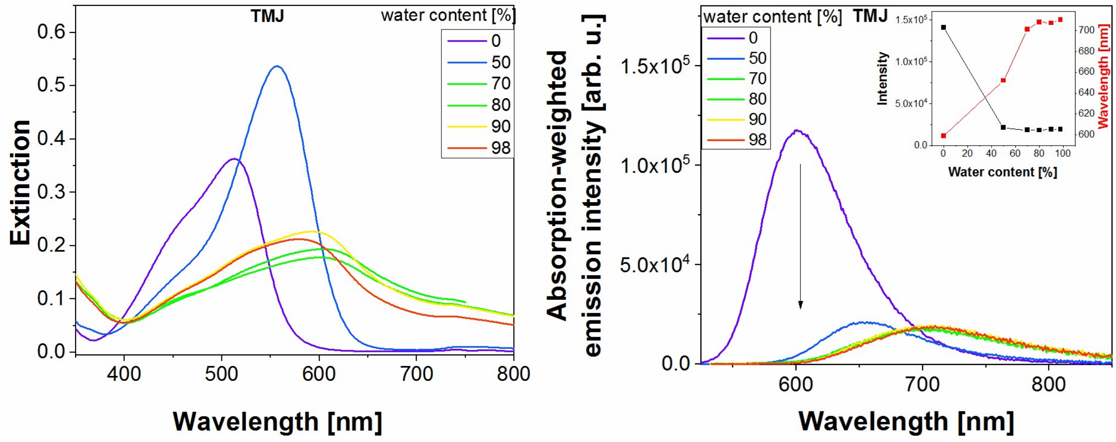


Figure S17. Absorption and absorption-weighted emission spectra (λ_{exc} = 513 nm) of TMJ (c = 7.5 µM) in dioxane-water mixtures with increasing water content.

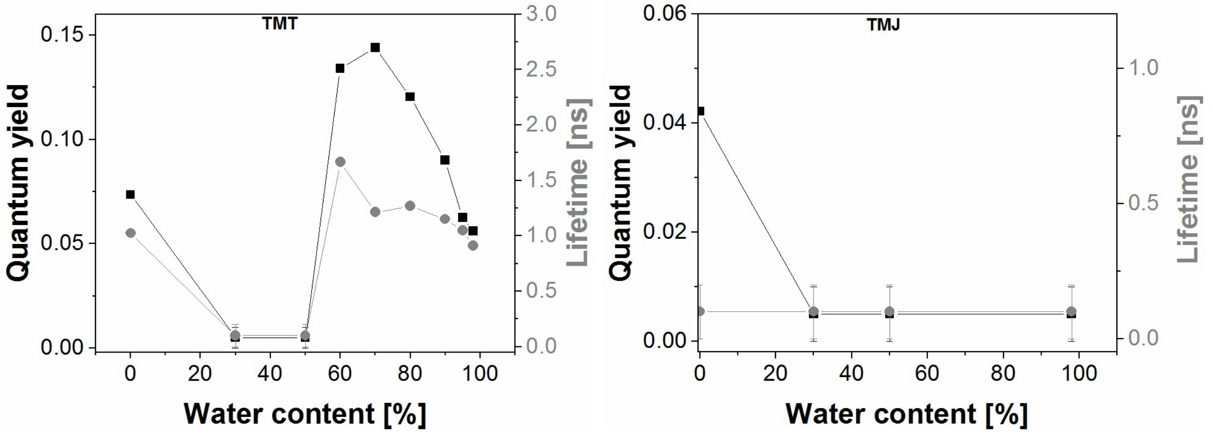


Figure S18. Fluorescence quantum yield (black symbols) and intensity-weighted lifetime (gray symbols) of TMT (right) and of TMJ (left) in dioxane-water mixtures with increasing water content.

Aggregate size.

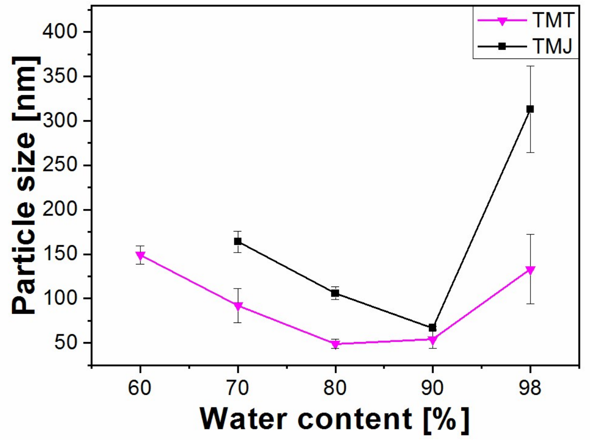


Figure S19. Size of the aggregates of the dyes formed after 10 min in ACN−water mixtures of varying water content determined by DLS.

IV XRD structure analysis of TMT and TMJ

Table S2. Summary of the crystal structure analysis of compounds TMT and TMJ.

Compound reference	TMT (wk244n)	TMJ (wk262)
Chemical formula	$C_{42.50}H_{31}ClN_4$	$C_{36}H_{30}N_4$
Formula Mass	633.16	518.64
Crystal system	Monoclinic'	Orthorhombic'
a/Å	9.7314(5)	12.7624(4)
b/Å	19.7804(10)	14.2194(4)
c/Å	18.0454(9)	30.1474(9)
α/°	90	90
β/°	101.472(2)	90
γ/°	90	90
Unit cell volume/Å^3	3404.2(3)	5471.0(3)
Temperature/K	150(2)	150(2)
Space group	$P2_1$	*Pbca*
No. of formula units per unit cell, *Z*	4	8
Radiation type	MoKα	MoKα
Absorption coefficient, μ/mm^{-1}	0.149	0.075
No. of reflections measured	81771	43876
No. of independent reflections	16916	6764
R_{int}	0.1766	0.1012
Final R_1 values ($I > 2\sigma(I)$)	0.0584	0.0656
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1547	0.1216
Final R_1 values (all data)	0.0619	0.1071
Final $wR(F^2)$ values (all data)	0.1584	0.1376
Goodness of fit on F^2	1.008	1.077
CCDC	1830876	1830877

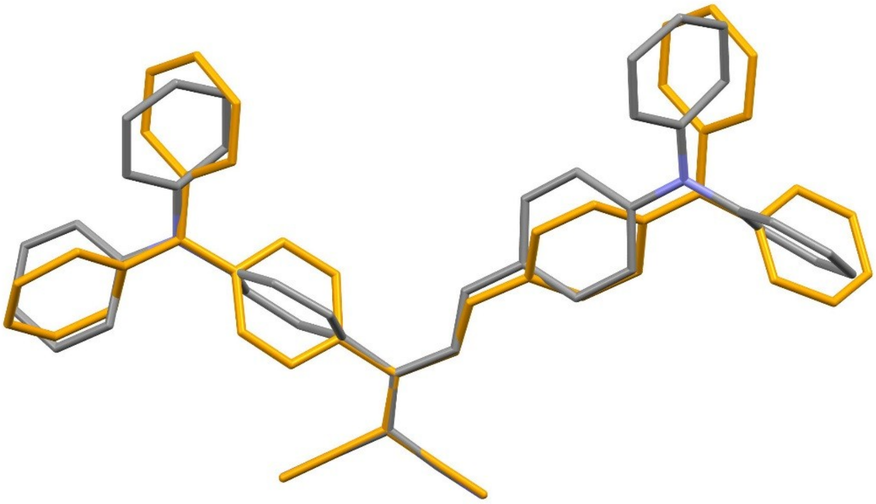


Figure S20. Overlay of the two symmetry independent forms of TMT showing the different conformations.

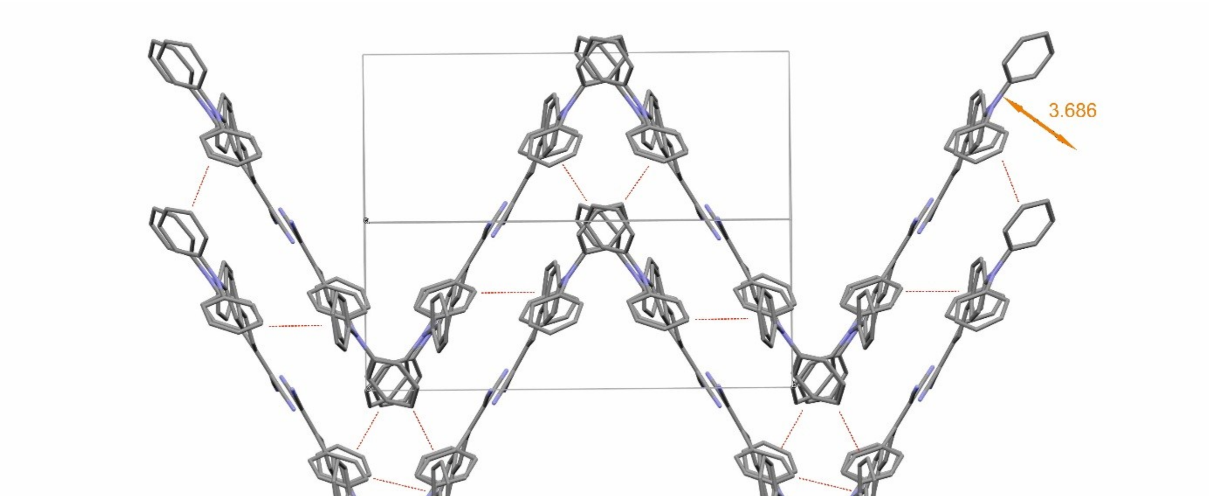


Figure S21. Arrangement of the molecules in a zigzag manner in the crystal packing of TMT with a distance of the layers of 3.686 Å and C-H···π interactions occurring between the layers (red dotted lines). H-atoms were omitted for clarity reasons.

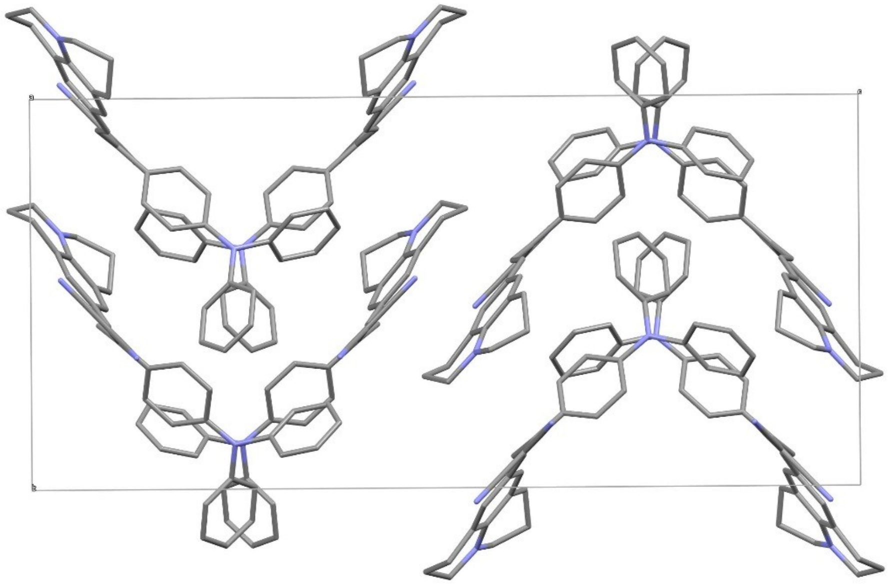


Figure S22. Arrangement of the TMJ molecules in the unit cell viewed along the a-axis; H-atoms were omitted for clarity reason.

V TMT in a polymer matrix

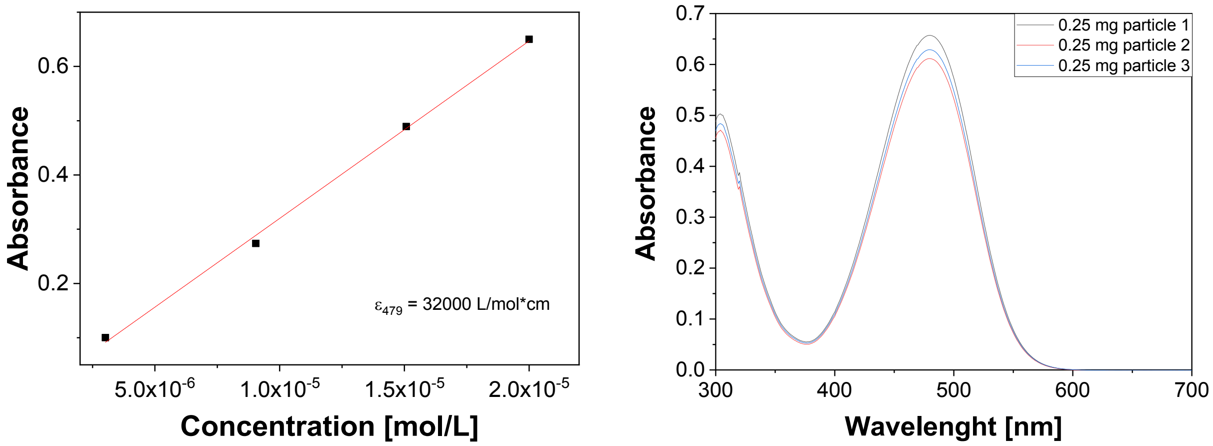


Figure S23. Left: Calibration curve for TMT in THF yielding a linear dependence of absorbance on dye concentration from a the molar absorption coefficient, ε of TMT in THF was determined to 32,000 L/mol*cm; Right: Absorption spectra of 0.25 mg PSP stained with TMT dissolved in THF; the measurements were done in triplicate to calculate a relative standard deviation.

(S1) T. V. U. Gangan, M. L. P. Reddy, *Dalton Trans.* **2015**, *44*, 15924–15937.

(S2) L. Rejc, L. Šmid, V. Kepe, Č. Podlipnik, A. Golobič, M. Bresjanac, J. R. Barrio, A. Petrič, J. Košmrlj, *J. Med. Chem.* **2017**, *60*, 8741−8757.

(S3) V. D. Gupta, A. B. Tathe, V. S. Padalkar, P. G. Umape, N. Sekar, *Dyes Pigm.* **2013**, *97*, 429–439.