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Electronic Supporting Information

Bis(Tercarbazole) Pyrene and Tetrahydropyrene Derivatives: Photophysical and Electrochemical Properties, Theoretical Modeling, and OLEDs

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Photophysical studies.

The orientation polarizability Δf is calculated as follows

$$\Delta_f = \left(\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right)$$

Where ε is the dielectric constant and n is the refractive index.

The $E_T(30)$ values in kcal.mol^{-1} and the normalized E_T^N values define the empirical solvent polarity scale.[1]

The emission quantum yield (ϕ) is calculated as follows

$$\emptyset = \emptyset_{std} \frac{F}{F_{std}} \frac{A_{std}}{A} \frac{n^2}{n_{std}^2}$$

Where F is the integrated intensity of the emission spectrum, A is the absorption, and n is the refractive index of the solvent used. The subscript "*std*" indicates that the corresponding parameter corresponds to the standard (9,10-diphenylanthracene in cyclohexane with a quantum yield of 1.00).

The radiative (k_r) and non-radiative (k_{nr}) decay constants were calculated as follows

$$k_r = \frac{\emptyset}{\tau}$$

$$k_{nr} = \frac{1 - \emptyset}{\tau}$$

The pure radiative lifetime (natural lifetime τ_n) is calculated as follows

$$\tau_n = \frac{\tau}{\emptyset}$$

Table S1. Fluorescence lifetimes, emission quantum yields, radiative and non-radiative decay rate constants and the natural lifetimes of compound **1** in different solvents.[1]

Compound	Solvent	τ_1 , ns (%)	τ_2 , ns (%)	τ_{avg} , ns	χ^2	ϕ_F	k_r (10^8) s^{-1}	k_{nr} (10^8) s^{-1}	τ_n , ns
1	Acetonitrile	2.1 (79)	10.00 (20)	3.7	1.1	0.70	1.90	0.81	5.3
	Cyclohexane	1.5 (66)	8.90 (34)	4.0	1.6	0.25	0.63	1.90	16.0
	DCM	1.9 (47)	9.00 (52)	5.6	1.4	0.43	0.77	1.00	13.0
	DMF	2.0 (56)	0.12 (43)	1.2	1.5	0.69	5.80	2.60	1.7
	Ethanol	2.0 (47)	9.60 (53)	6.0	1.6	0.58	0.97	0.70	10.0
	Hexane	1.4 (70)	5.60 (30)	2.7	1.6	0.82	3.10	0.68	3.2
	THF	1.9 (42)	9.30 (58)	6.2	1.4	0.43	0.70	0.93	14.0

τ =fluorescence lifetime, τ_{avg}=average fluorescence lifetime, $_{\Phi F}$=fluorescence quantum yield; k_r=radiative rate constant; k_{nr}=non-radiative rate constant, τ_n=natural fluorescence lifetime.

Table S2. Fluorescence lifetimes, emission quantum yields, radiative and non-radiative decay rate constants and the natural lifetimes of compound **2** in different solvents.[1]

Compound	Solvent	τ , ns	χ^2	ϕ_F	k_r (10^7) s^{-1}	k_{nr} (10^7) s^{-1}	τ_n , ns
2	Acetonitrile	12	1.7	0.14	1.2	7.2	85
	Cyclohexane	18	2.4	0.49	2.7	2.8	37
	DCM	23	2.5	0.56	2.5	1.9	40
	DMF	19	1.6	0.42	2.2	3.1	45
	Ethanol	17	1.9	0.51	3.0	2.8	34
	Hexane	11	1.7	0.27	2.4	6.5	41
	THF	18	2.1	0.40	2.2	3.3	45

τ =fluorescence lifetime, $_{\Phi F}$=fluorescence quantum yield; k_r=radiative rate constant; k_{nr}=non-radiative rate constant, τ_n=natural fluorescence lifetime.

Table S3. Fluorescence lifetimes, emission quantum yields, radiative and non-radiative decay rate constants and the natural lifetimes of compound **3** in different solvents.

Compound	Solvent	τ1 , ns (%)	τ2 , ns (%)	τavg , ns	χ^2	ϕ_F	*k*r (10^8) s^{-1}	*k*nr (10^8) s^{-1}	τn , ns
3	Acetonitrile	7.0	--	7.0	2.0	0.39	0.56	0.88	18
	Chloroform	1.1 (80)	1.8 (20)	1.2	1.3	0.07	0.57	7.60	17
	Cyclohexane	4.7	--	4.7	1.7	0.25	0.53	1.60	19
	DMF	5.0 (10)	6.5 (90)	6.3	1.9	0.34	0.54	1.00	19
	DMSO	4.3 (10)	6.5 (90)	6.3	1.8	0.40	0.63	0.95	16
	1,4-dioxane	4.4 (10)	5.4 (90)	5.3	1.6	0.24	0.45	1.40	22
	Ethanol	5.9	--	5.9	1.6	0.29	0.49	1.20	20
	Ethyl acetate	5.9 (80)	4.9 (20)	5.7	1.7	0.30	0.52	1.20	19
	THF	3.7 (10)	4.7 (90)	4.7	1.7	0.23	0.49	1.60	20

τ =fluorescence lifetime, τ_{avg}=average fluorescence lifetime, $_{\Phi F}$=fluorescence quantum yield; k_r=radiative rate constant; k_n=non-radiative rate constant, τ_n=natural fluorescence lifetime.

Table S4. Fluorescence lifetimes, emission quantum yields, radiative and non-radiative decay rate constants and the natural lifetimes of compound **4** in different solvents.

Compound	Solvent	τ1 , ns (%)	τ2 , ns (%)	τavg , ns	χ^2	ϕ_F	*k*r (10^7) s^{-1}	*k*nr (10^7) s^{-1}	τn , μs
4	Acetonitril	16 (100)	--	16	2.4	0.03	0.18	6.0	0.54
	Chlorofor	22 (40)	32 (60)	28	1.9	0.13	0.46	3.1	0.22
	Cyclohexa	10. (10)	22 (90)	21	1.9	0.26	1.20	3.5	0.08
	DMF	17 (100)	--	17	1.6	0.08	0.48	5.5	0.21
	DMSO	11 (20)	19 (80)	17	1.6	0.04	0.23	5.5	0.43
	1,4-	44 (100)	--	44	3.0	0.34	0.78	1.5	0.13
	Ethanol	10 (10)	21 (90)	20.	1.7	0.05	0.24	4.6	0.41
	Ethyl	15 (10)	31 (90)	30.	2.1	0.08	0.27	3.1	0.37
	THF	14 (10)	29 (90)	28	1.8	0.13	0.46	3.1	0.22

τ =fluorescence lifetime, τ_{avg}=average fluorescence lifetime, $_{\Phi F}$=fluorescence quantum yield; k_r=radiative rate constant; k_{nr}=non-radiative rate constant, τ_n=natural fluorescence lifetime.

Table S5. Fluorescence lifetimes, emission quantum yields, radiative and non-radiative decay rate constants and the natural lifetimes of

compound **5** in different solvents.

Compound	Solvent	τ1 , ns (%)	τ2 , ns (%)	τavg , ns	χ^2	ϕ_F	*k*r (10^7) s^{-1}	*k*nr (10^7) s^{-1}	τn ,
5	Acetonitrile	11.00	--	11.00	1.5	0.48	4.4	4.8	23
	Chloroform	0.49	--	0.49	1.3	0.04	8.2	190.0	12
	Cyclohexane	9.00 (80)	11.0 (20)	9.30	1.4	0.20	2.1	8.6	47
	DMF	4.70 (10)	8.1 (90)	7.90	1.6	0.37	4.7	8.0	21
	DMSO	7.30 (20)	9.3 (80)	9.00	1.5	0.44	4.9	6.2	20.
	1,4-dioxane	8.30 (40)	10.0 (60)	9.60	1.5	0.58	6.1	4.4	16
	Ethanol	6.80 (10)	10.0 (90)	9.80	1.4	0.46	4.7	5.5	21
	Ethyl acetate	7.60 (10)	10.0 (90)	10.00	1.4	0.50	4.9	4.9	20
	THF	9.90	--	9.90	1.4	0.52	5.2	4.8	19

τ =fluorescence lifetime, τ_{avg}=average fluorescence lifetime, $_{\Phi F}$=fluorescence quantum yield; k_r=radiative rate constant; k_n=non-radiative rate constant, τ_n=natural fluorescence lifetime.

Table S6. Fluorescence lifetimes, emission quantum yields, radiative and non-radiative decay rate constants and the natural lifetimes of compound **6** in different solvents.

Compound	Solvent	τ1 , ns (%)	τ2 , ns (%)	τavg , ns	χ^2	ϕ_F	*k*r (10^7) s^{-1}	*k*nr (10^7) s^{-1}	τn , ns
6	Acetonitrile	7.6	--	7.6	1.6	0.40	5.3	7.9	19
	Chloroform	1.2	--	1.2	2.2	0.06	5.0	78.0	20.
	Cyclohexane	5.4	--	5.4	1.5	0.18	3.3	15.0	30.
	DMF	2.6 (20)	6.8 (80)	6.0	1.6	0.32	5.3	11.0	19
	DMSO	7.0	--	7.0	1.6	0.32	4.6	9.7	22
	1,4-dioxane	4.7 (10)	6.0 (90)	5.8	1.6	0.37	6.3	11.0	16
	Ethanol	6.4	--	6.4	1.6	0.32	5.0	11.0	20.
	Ethyl acetate	6.2	--	6.2	1.5	0.35	5.6	10.0	18
	THF	6.2	--	6.2	1.7	0.41	6.6	9.6	15

τ =fluorescence lifetime, τ_{avg}=average fluorescence lifetime, $_{\Phi F}$=fluorescence quantum yield; k_r=radiative rate constant; k_{nr}=non-radiative rate constant, τ_n=natural fluorescence lifetime

Table S7. Absorption and emission maxima with the Stokes shifts in different solvents for compounds **1 – 6.**

Compound	Solvent	λ_{max}^{em}, nm	λ_{max}^{abs}, nm	$\Delta\bar{\nu}$, cm^{-1}	$\Delta\bar{\nu}$, eV
1	Acetonitrile	390	349	3010	0.37
	Cyclohexane	365	351	1090	0.14
	DCM	384	348	2690	0.33
	DMF	389	349	2950	0.37
	Ethanol	385	349	2680	0.33
	Hexane	364	351	1020	0.13
	THF	372	350	1690	0.21
2	Acetonitrile	451	341	7150	0.89
	Cyclohexane	423	344	5430	0.67
	DCM	445	344	6600	0.82
	DMF	450	341	7100	0.88
	Ethanol	442	340	6790	0.84
	Hexane	422	344	5370	0.67
	THF	436	344	6130	0.76
3	Acetonitrile	398	347	3690	0.46
	Chloroform	397	349	3460	0.43
	Cyclohexane	386	349	2750	0.34
	DMF	395	348	3420	0.42
	DMSO	399	348	3670	0.46
	1,4-Dioxane	391	348	3160	0.39
	Ethanol	393	346	3460	0.43
	Ethyl acetate	392	347	3310	0.41
	THF	392	347	3310	0.41
4	Acetonitrile	539	340	10800	1.30
	Chloroform	478	341	8400	1.00
	Cyclohexane	423	339	5860	0.73
	DMF	533	343	10400	1.30
	DMSO	537	344	10400	1.30
	1,4-Dioxane	449	341	7050	0.87
	Ethanol	509	340	9760	1.20
	Ethyl acetate	483	341	8620	1.10
	THF	490	340	9000	1.10
5	Acetonitrile	373	347	2010	0.25
	Chloroform	372	349	1770	0.22
	Cyclohexane	369	347	1720	0.21
	DMF	373	347	2010	0.25
	DMSO	375	348	2070	0.26
	1,4-Dioxane	372	347	1940	0.24
	Ethanol	371	347	1860	0.23
	Ethyl acetate	371	347	1860	0.23
	THF	372	347	1940	0.24
6	Acetonitrile	405	348	4040	0.50
	Chloroform	399	349	3590	0.45

	Cyclohexane	385	348	2760	0.34
	DMF	406	349	4020	0.50
	DMSO	406	350	3940	0.49
	1,4-Dioxane	390	349	3010	0.37
	Ethanol	403	347	4000	0.50
	Ethyl acetate	392	348	3220	0.40
	THF	392	348	3220	0.40

λ_{max}^{em}=longest wavelength of emission; λ_{max}^{abs} longest wavelength of absorption; $\boldsymbol{\Delta\bar{\nu}}$=Stokes shift;

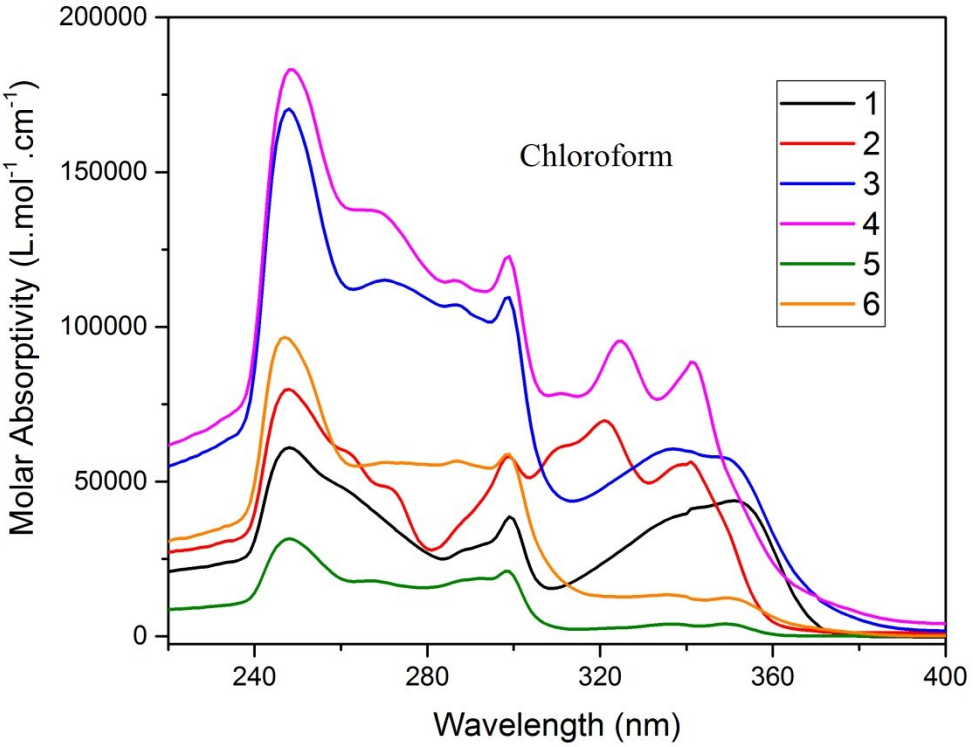


Figure S1. Molar absorptivity of compounds **1 - 6** in chloroform.

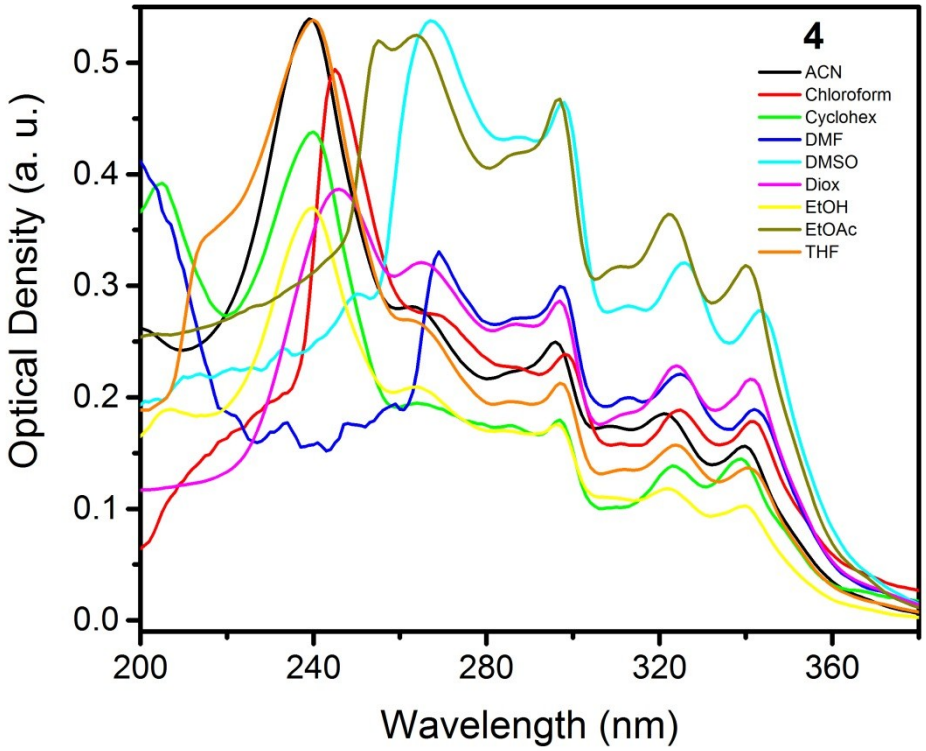


Figure S2. Absorption spectra of compound **4** in different solvents.

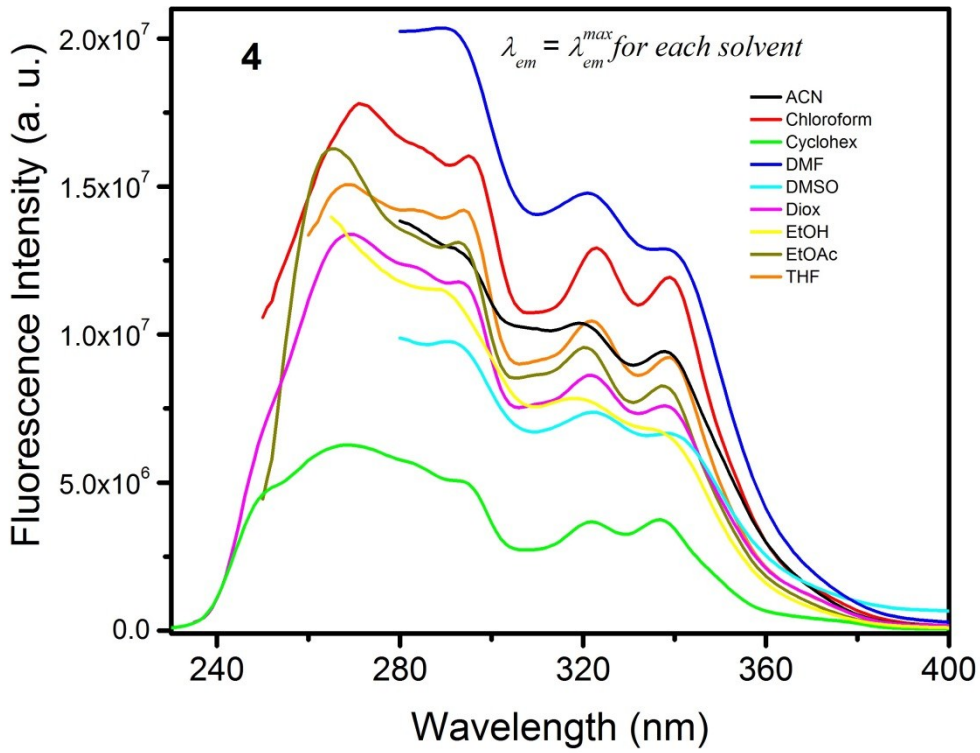


Figure S3. Excitation spectra of compound **4** in different solvents.

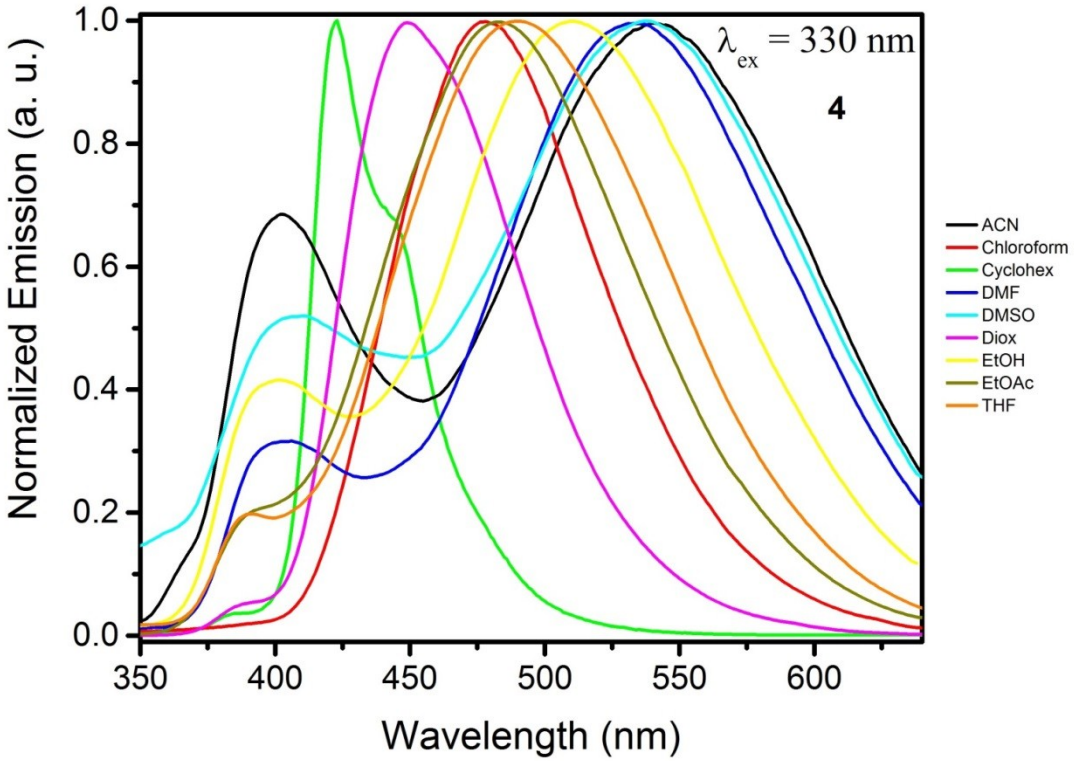


Figure S4. Normalized emission spectra of compound **4** in nine different solvents.

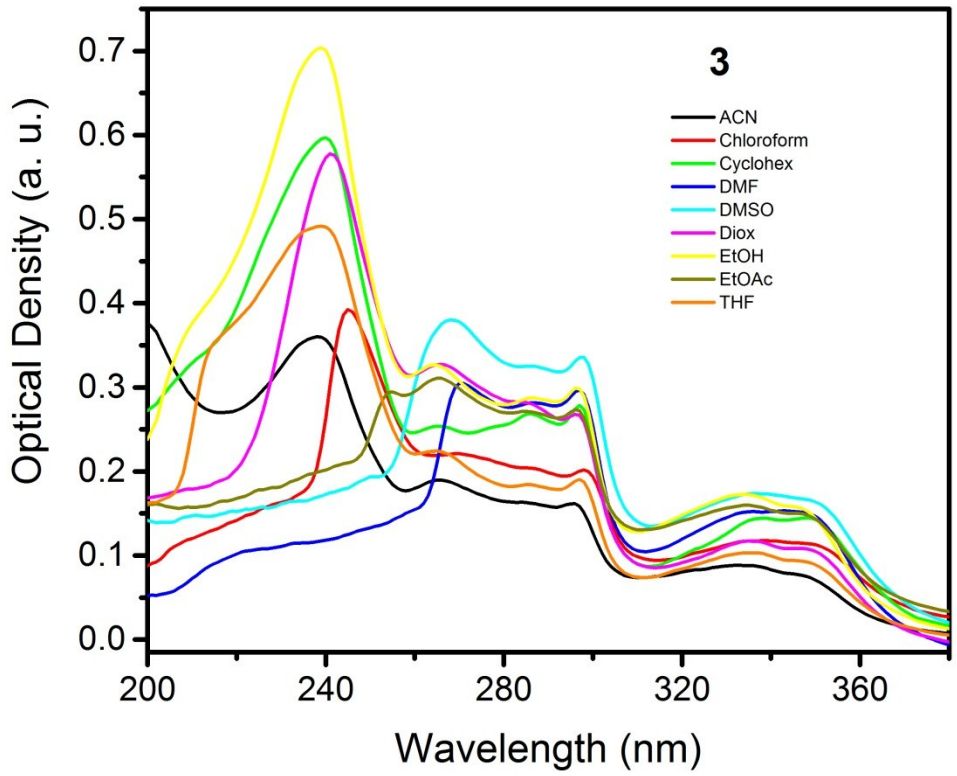


Figure S5. Absorption spectra of compound **3** in different solvents.

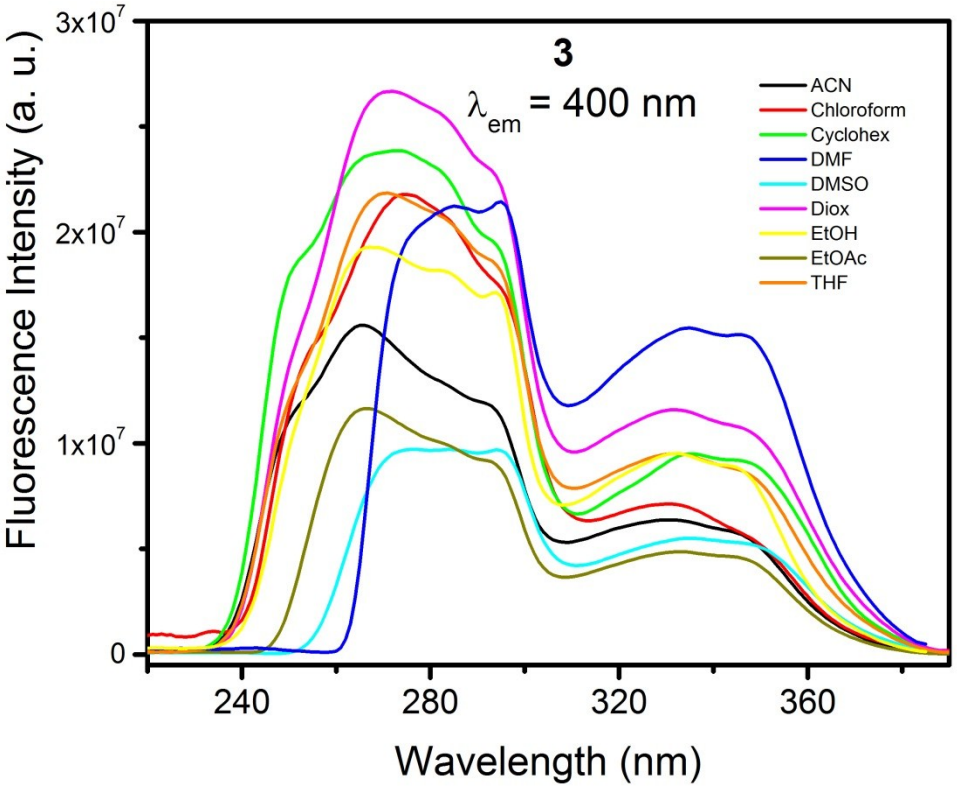


Figure S6. Excitation spectra of compound **3** in different solvents.

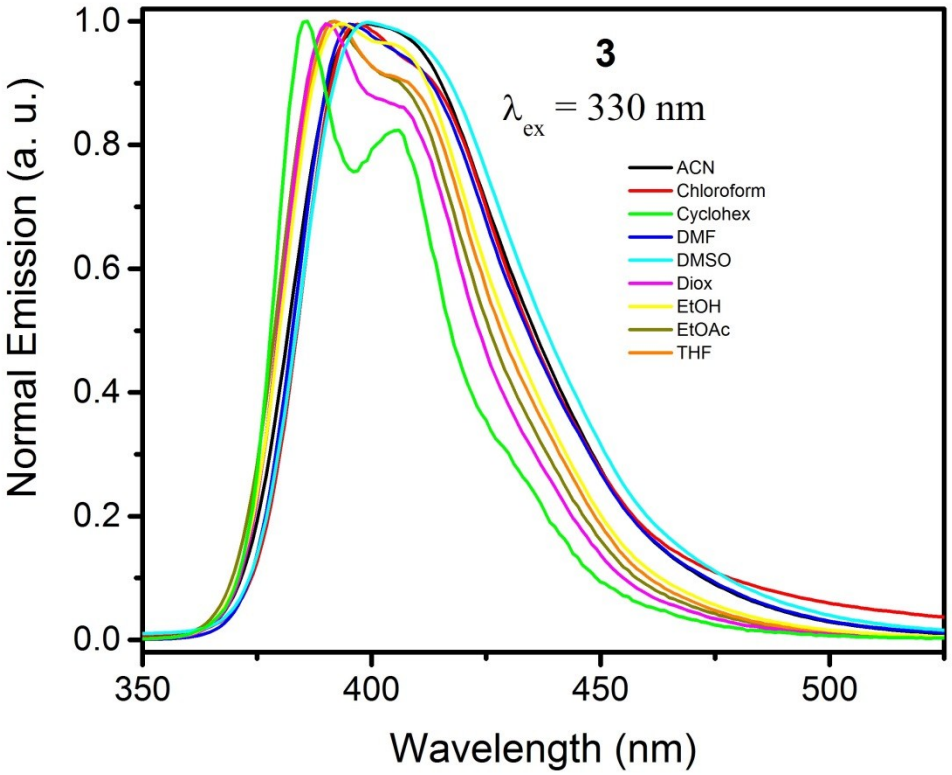


Figure S7. Normalized emission spectra of compound **3** in different solvents.

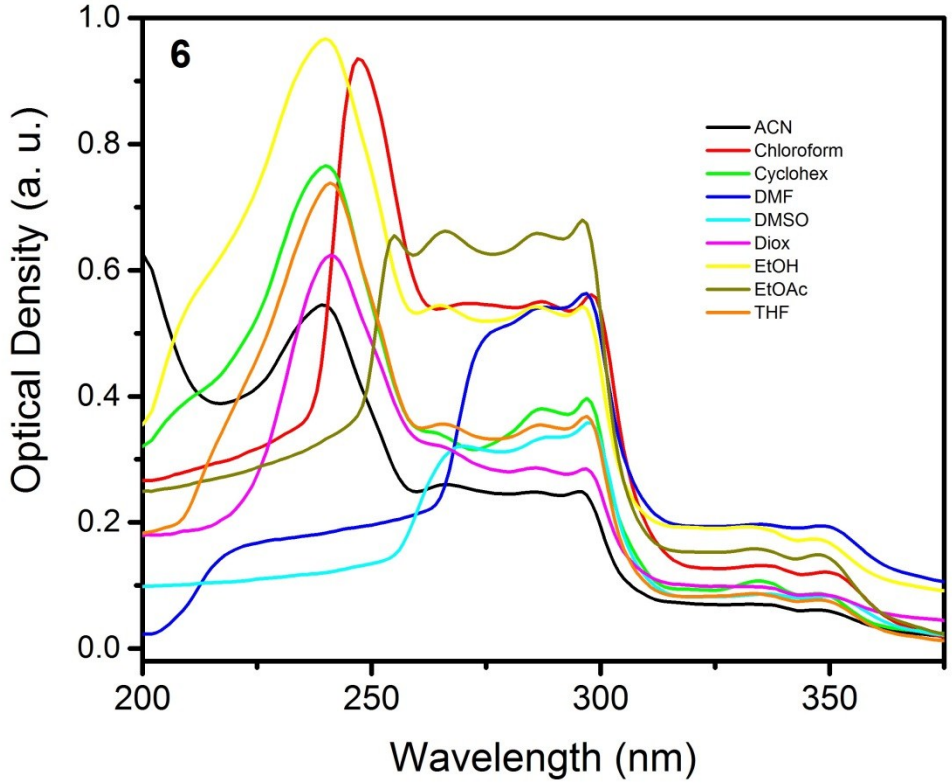


Figure S8. Absorption spectra of compound **6** in different solvents.

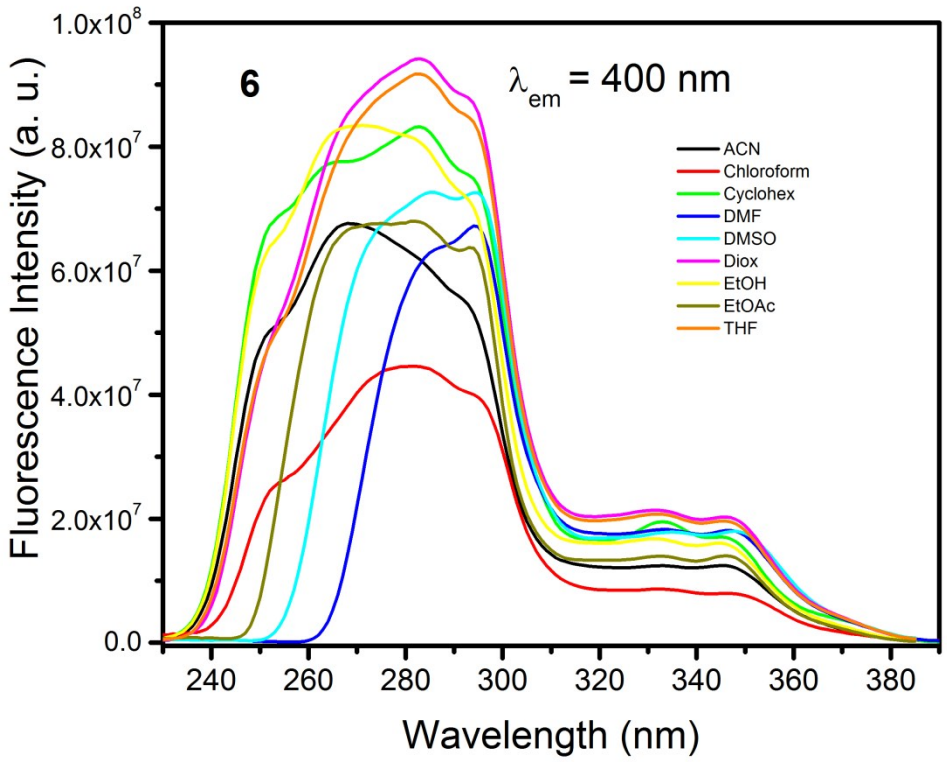


Figure S9. Excitation spectra of compound **6** in different solvents.

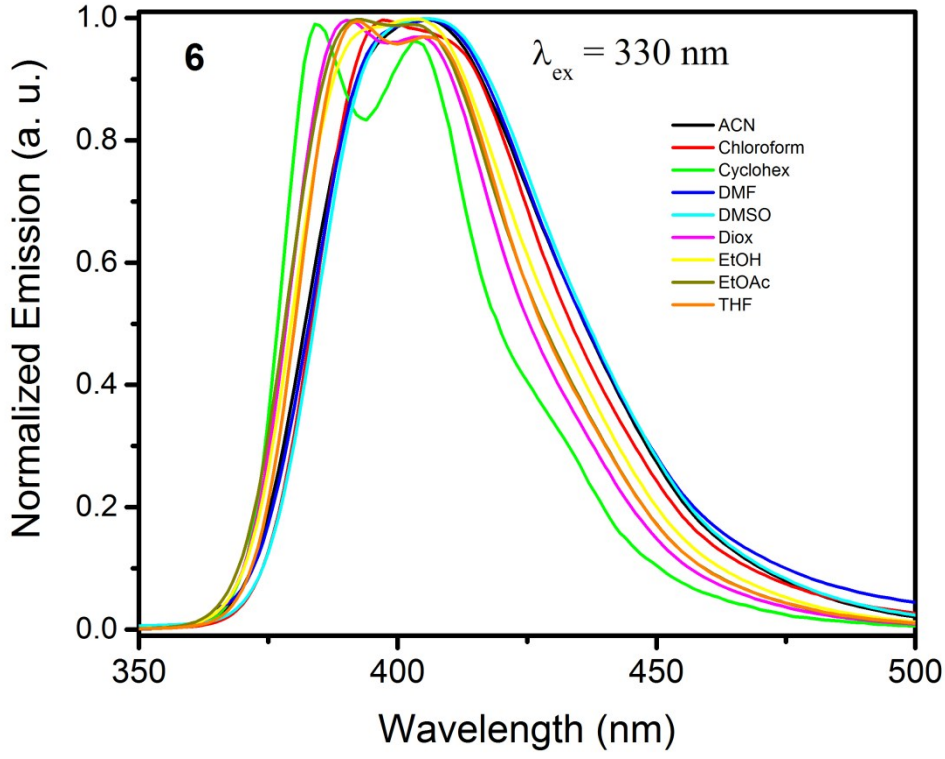


Figure S10. Normalized emission spectra of compound **6** in different solvents.

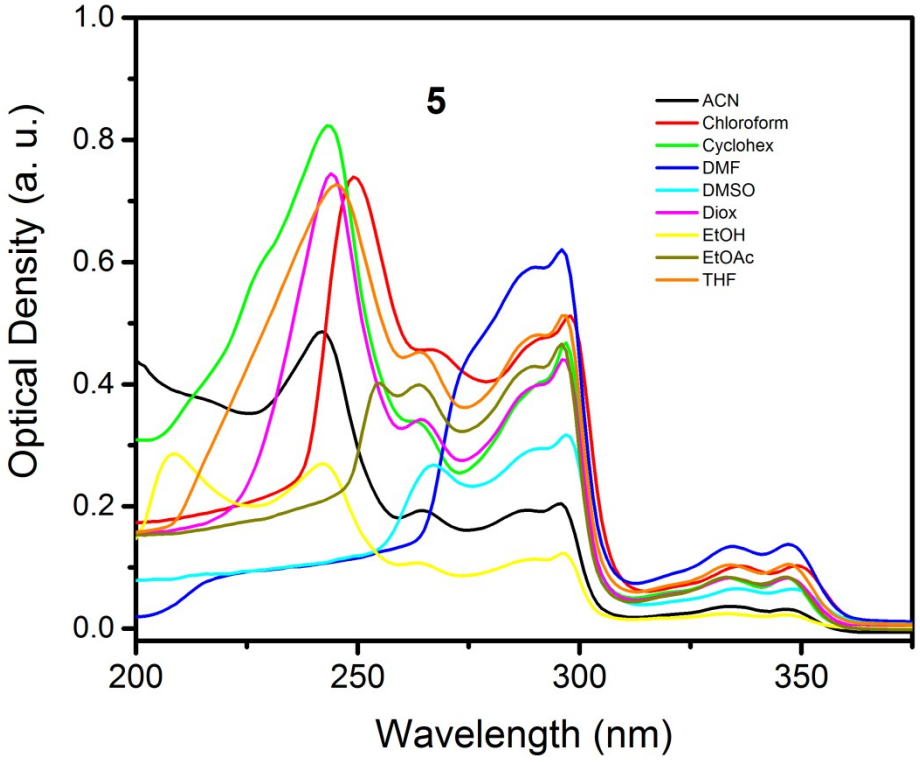


Figure S11. Absorption spectra of compound **5** in different solvents.

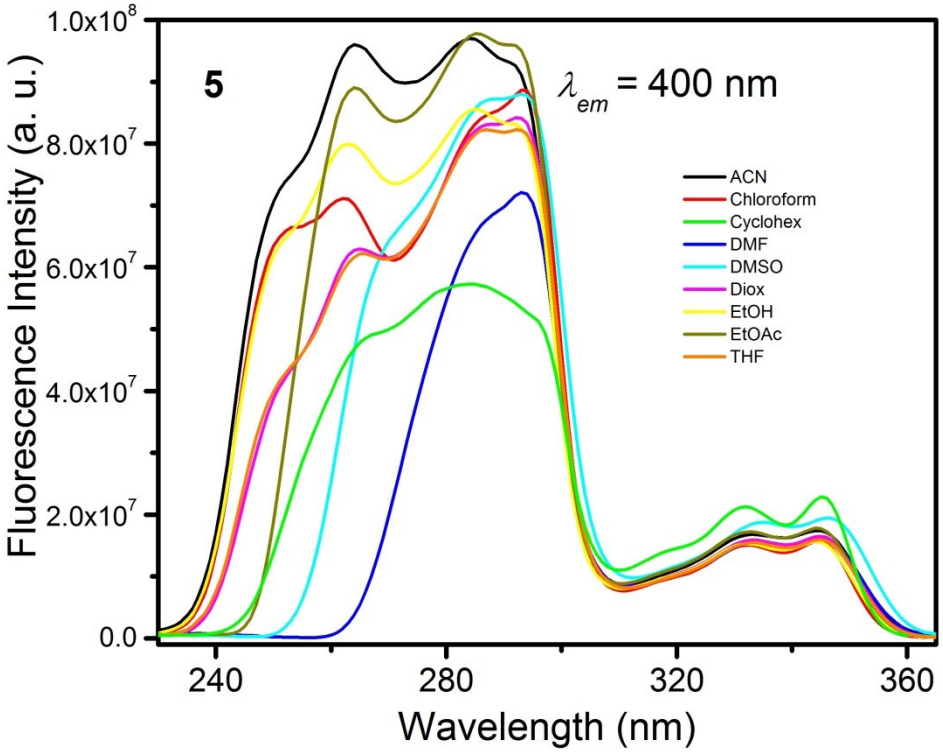


Figure S12. Excitation spectra of compound **5** in different solvents.

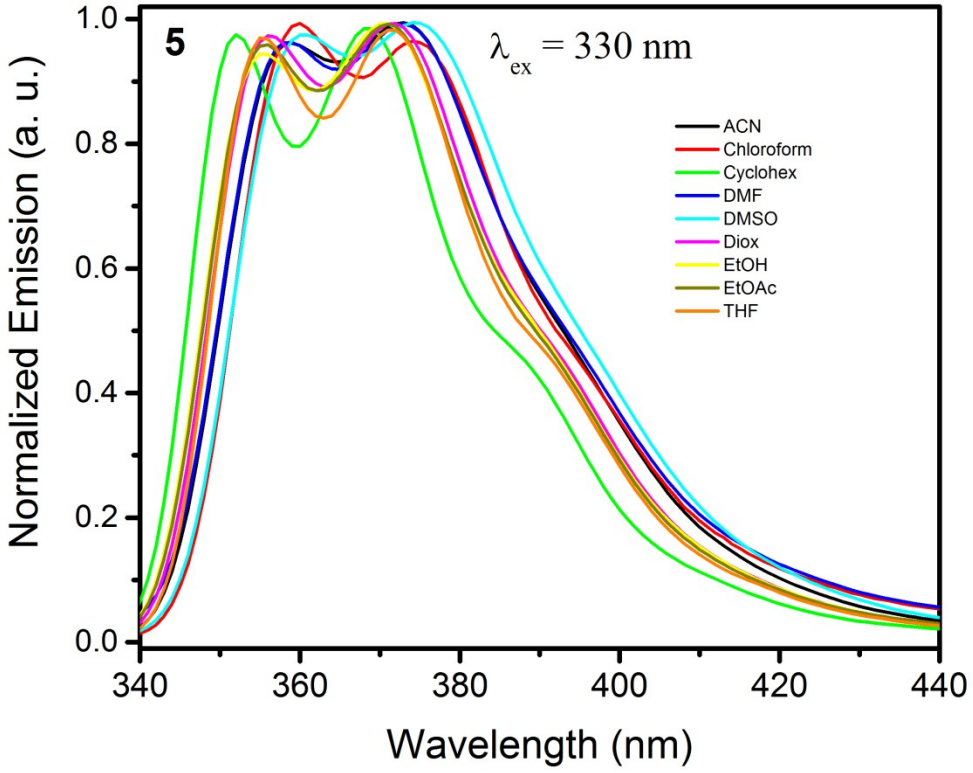


Figure S13. Normalized emission spectra of compound **5** in different solvents.

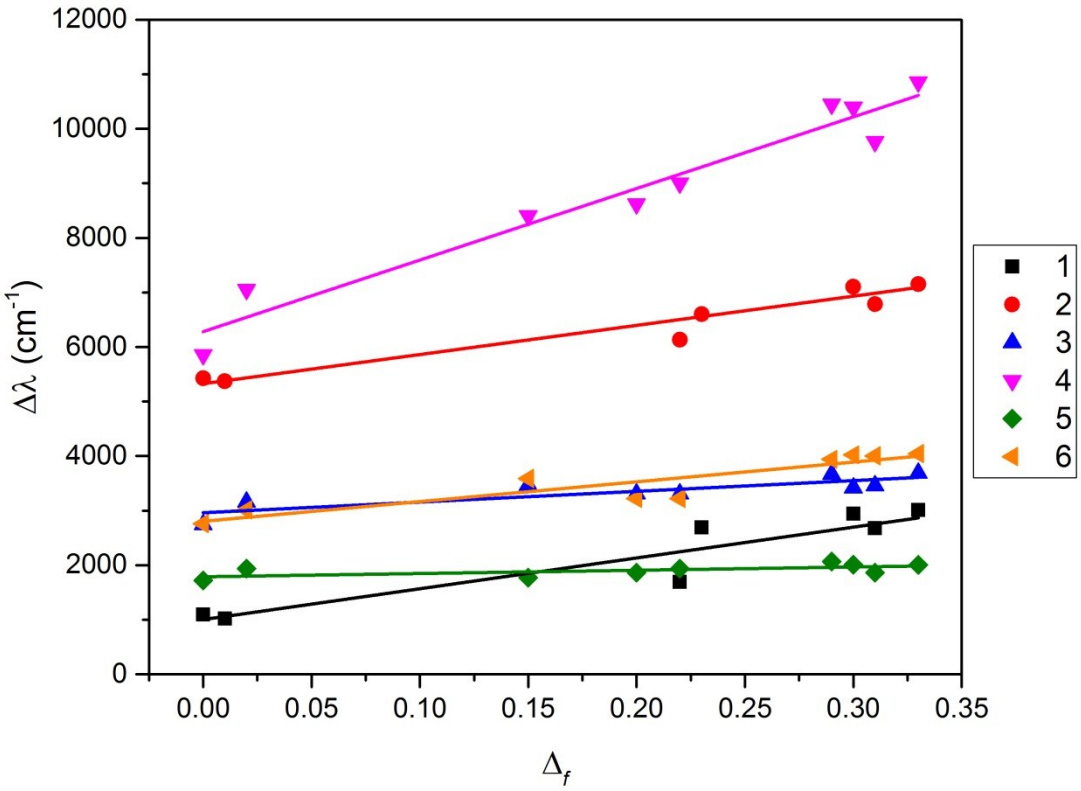


Figure S14. Stokes shifts vs. orientation polarizability for compounds **1** – **6.**

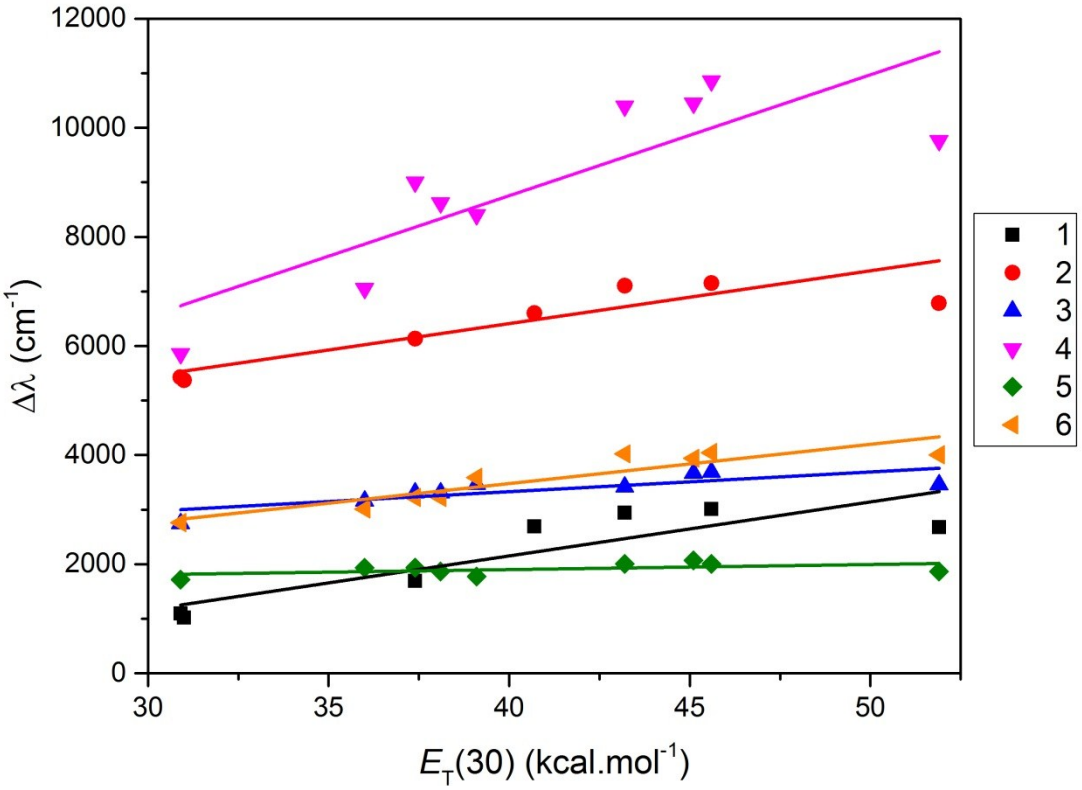


Figure S15. Stokes shifts vs. empirical solvent polarity for compounds **1 – 6.**

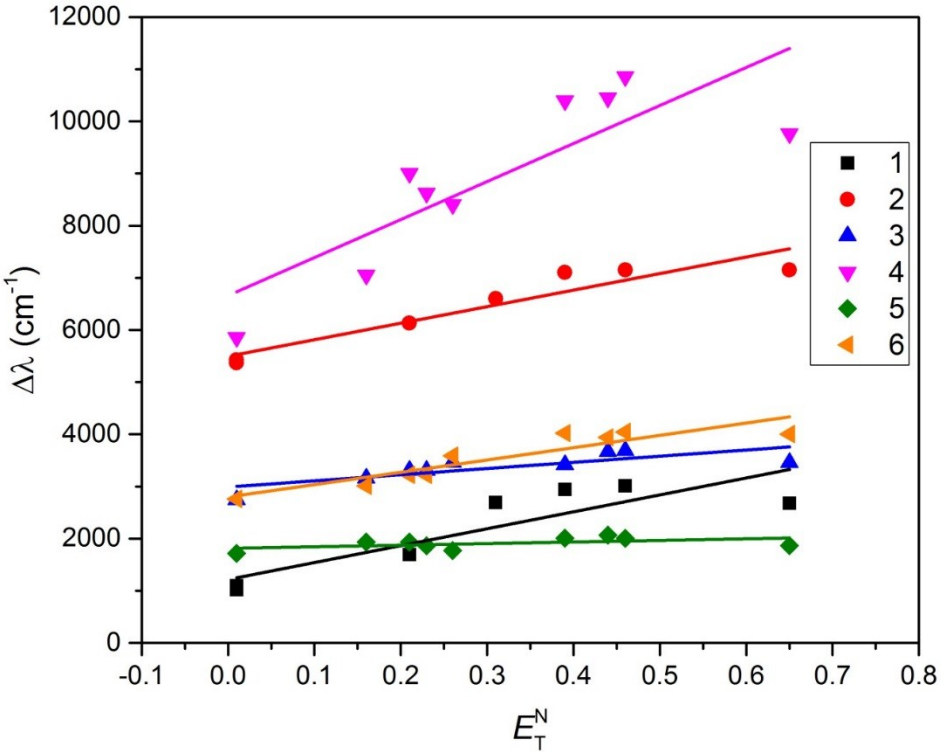
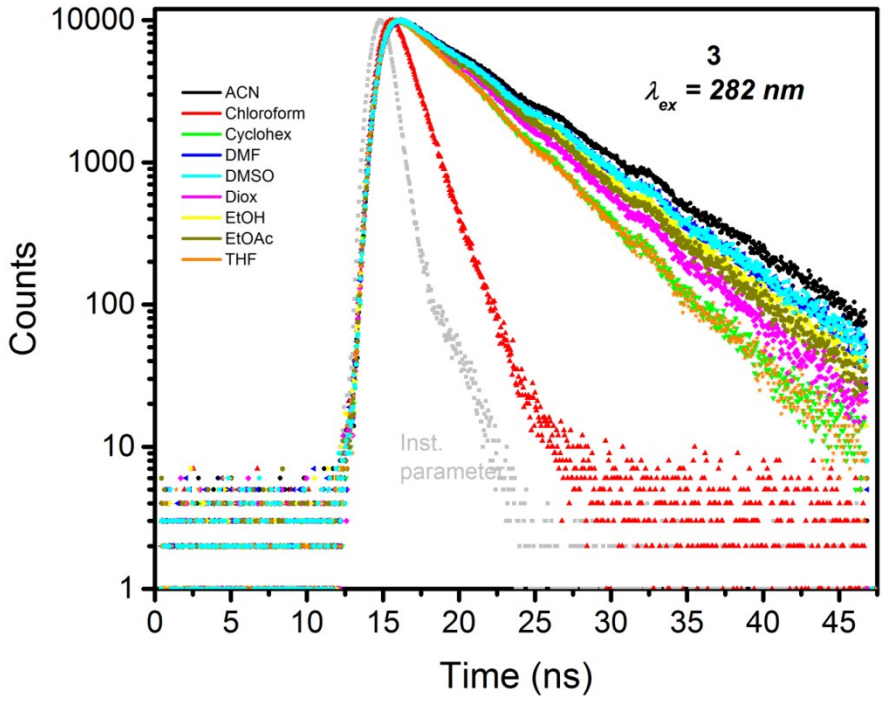


Figure S16. Stokes shifts vs. normalized empirical solvent polarity for compounds **1 – 6**.



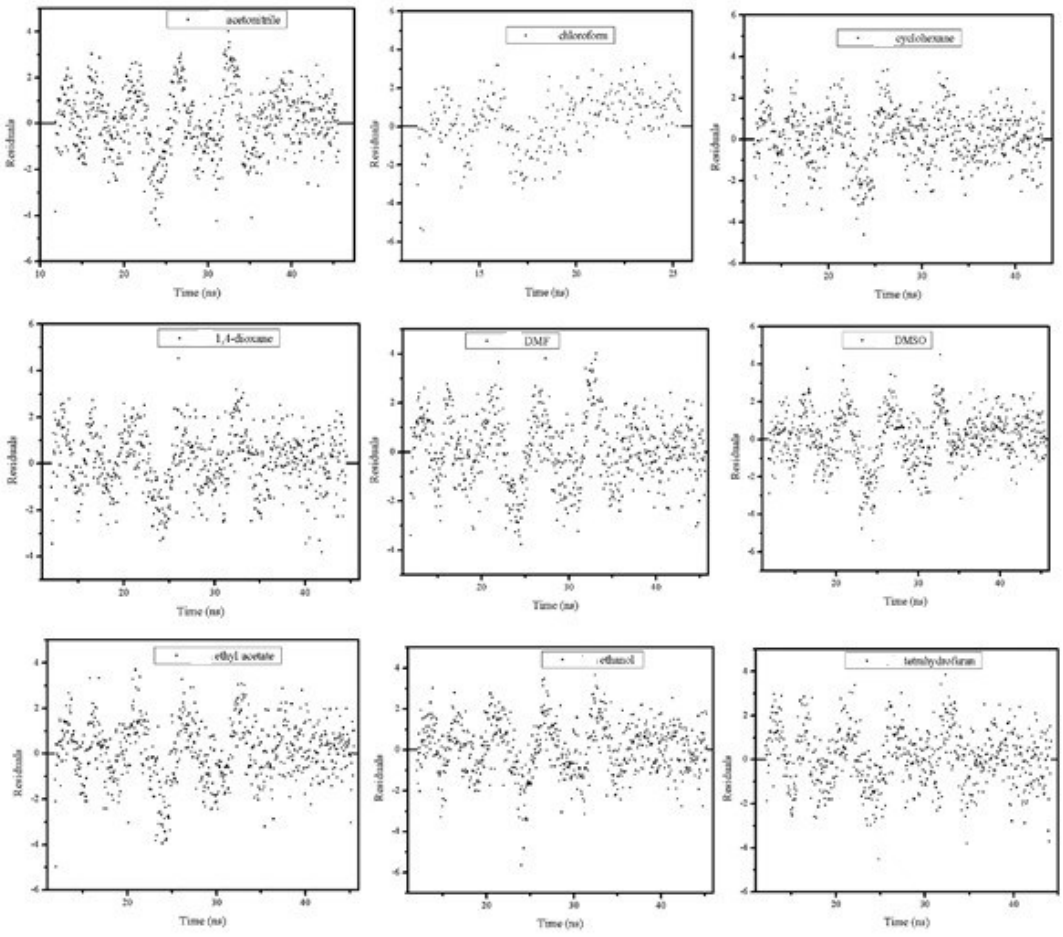


Figure S17. Lifetime decays of compound **3** in different solvents with the fitting and residuals.

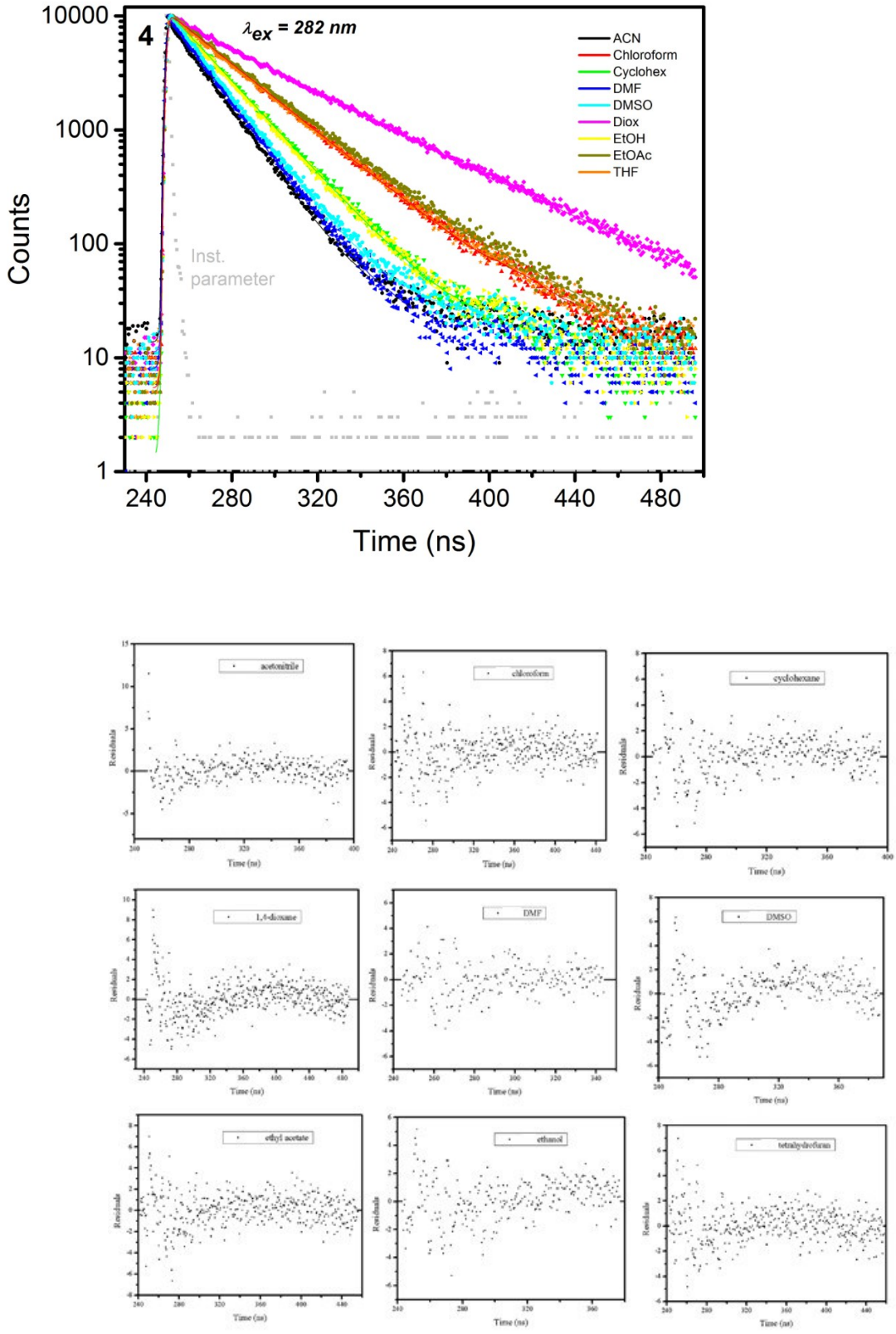


Figure S18. Lifetime decays of compound **4** in different solvents with the fitting and residuals.

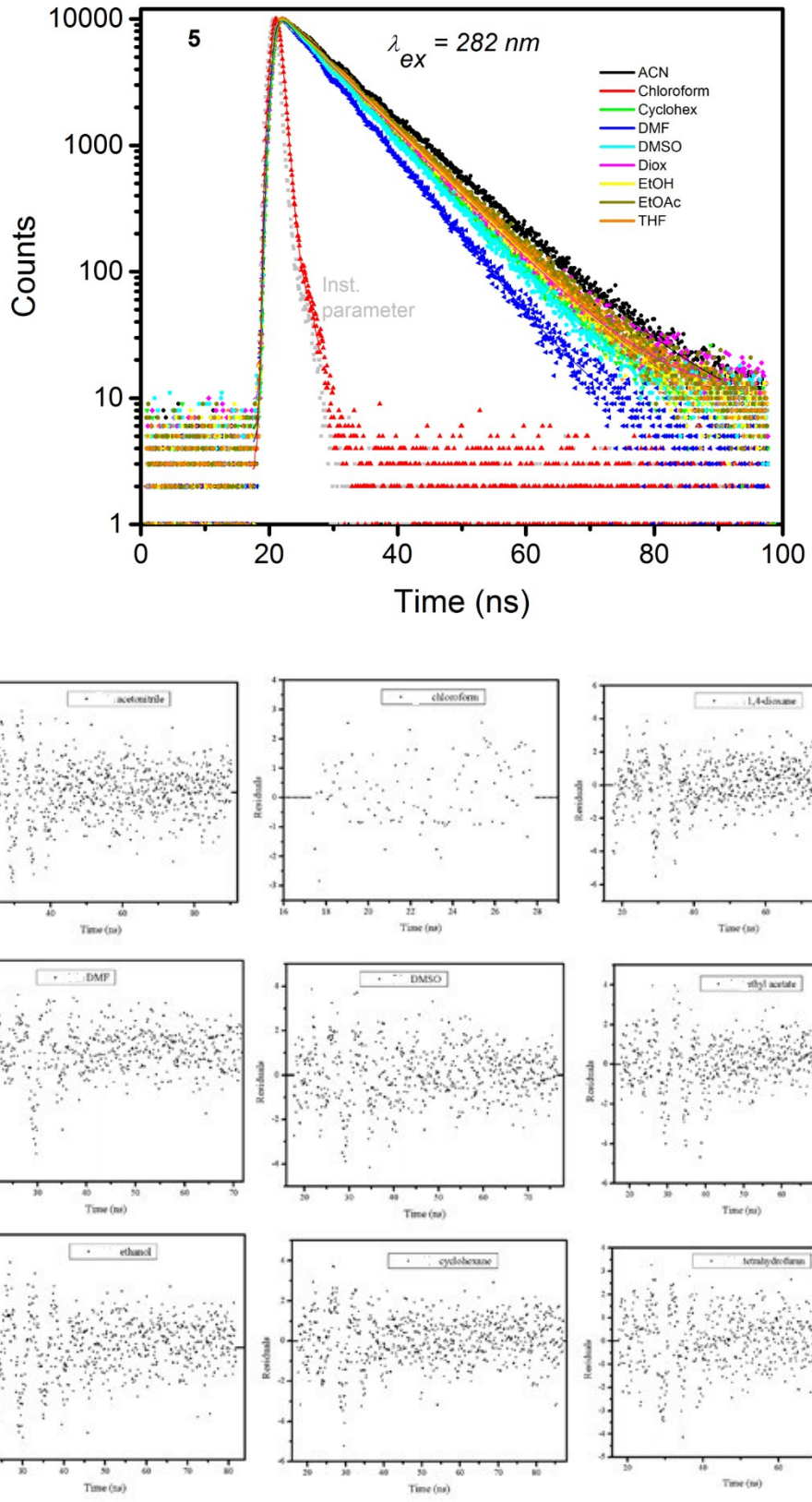


Figure S19. Lifetime decays of compound **5** in different solvents with the fitting and residuals.

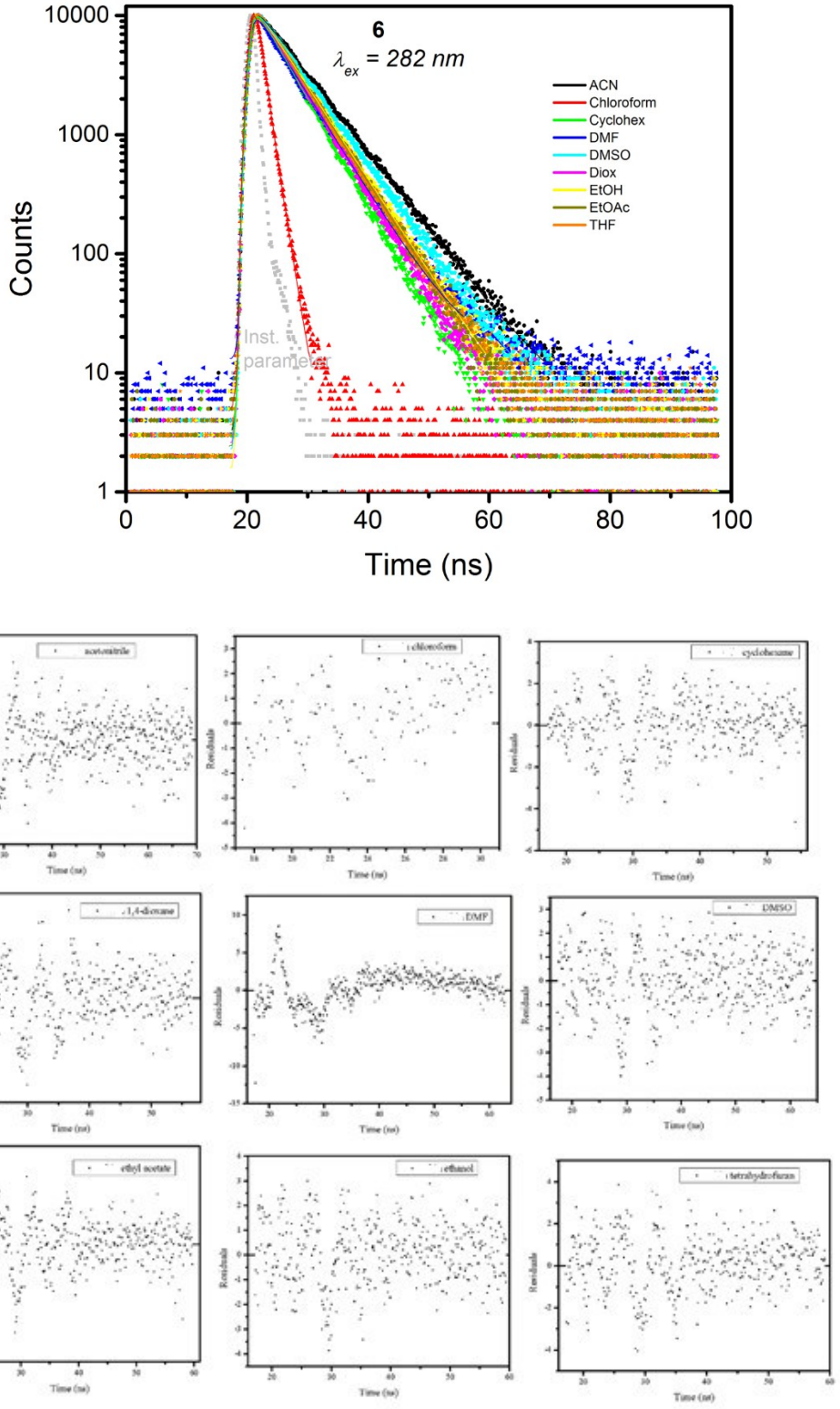


Figure S20. Lifetime decays of compound **6** in different solvents with the fitting and residuals.

Table S8. Properties of the solvents used in these solvatochromic studies (refractive index n, empirical solvent polarity E_T (30) and orientation polarizability Δf).

Solvent (Abbreviation)	n	E_T **(30) kcal.mol^{-1}**	E_T^N	Δf
Acetonitrile (ACN)	1.3415	45.6	0.46	0.33
Chloroform ($CHCl_3$)	1.4458	39.1	0.26	0.15
Cyclohexane (Cyclohex)	1.4262	30.9	0.01	0.00
Dichloromethane (DCM)	1.4241	40.7	0.31	0.23
N,N-Dimethylformamide (DMF)	1.4305	43.2	0.39	0.30
Dimethylsulfoxide (DMSO)	1.4793	45.1	0.44	0.29
1,4-Dioxane (Diox)	1.4224	36.0	0.16	0.02
Ethanol (EtOH)	1.3614	51.9	0.65	0.31
Ethyl acetate (EtOAc)	1.3724	38.1	0.23	0.20
Hexane (Hex)	1.3749	31.0	0.01	0.01
Tetrahydrofuran (THF)	1.4072	37.4	0.21	0.22

Chloroform								
#	λ_{max}^{em}**, nm**	λ_{max}^{abs}**, nm**	**Δλ, cm^{-1}**	**τ_F, ns**	**τ_n, ns**	**Φ_F**	**k_r , (10^7) s^{-1}**	**k_{nr} , (10^7) s^{-1}**
1	378	351	2030	1.40	24	0.06	4.10	65.0
2	443	341	6750	1.60	31	0.05	3.20	61.0
3	397	349	3460	1.20	17	0.07	5.70	76.0
4	478	341	8400	28.00	220	0.10	0.46	3.1
5	372	349	1770	0.49	12	0.04	8.20	190.0
6	399	349	3590	1.20	20.	0.06	5.00	78.0

THF								
#	λ_{max}^{em}**, nm**	λ_{max}^{abs}**, nm**	**Δλ, cm^{-1}**	**τ_F, ns**	**τ_n, ns**	**Φ_F**	**k_r , (10^7) s^{-1}**	**k_{nr} , (10^7) s^{-1}**
1	372	350	1690	6.2	14	0.43	7.00	9.3
2	436	344	6130	18.0	45	0.40	2.20	3.3
3	392	347	3310	4.7	20.	0.23	4.90	12.0
4	490	340	9000	28.0	220	0.13	0.46	3.1
5	372	347	1940	10.0	19	0.52	5.20	4.8
6	392	348	3220	6.2	15	0.41	6.60	9.6

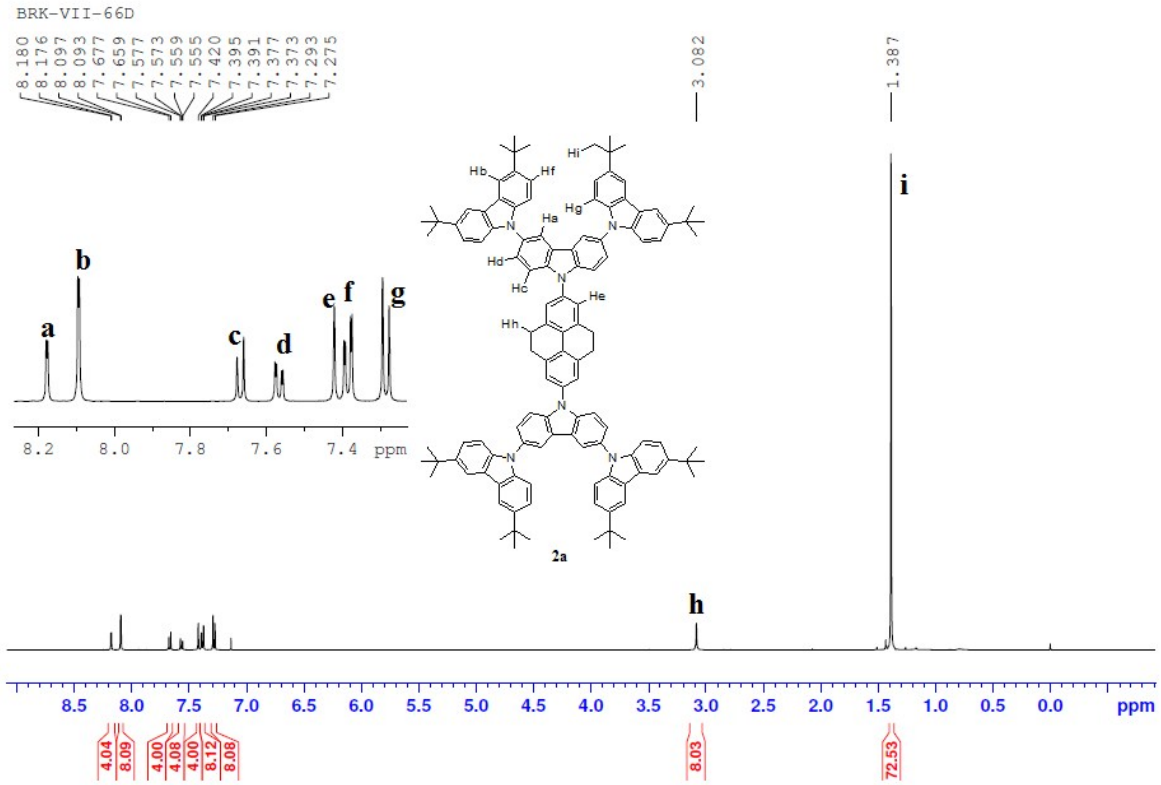


Figure S21. 500 MHz ^{1}H NMR of compound **3** in $CDCl_3$.

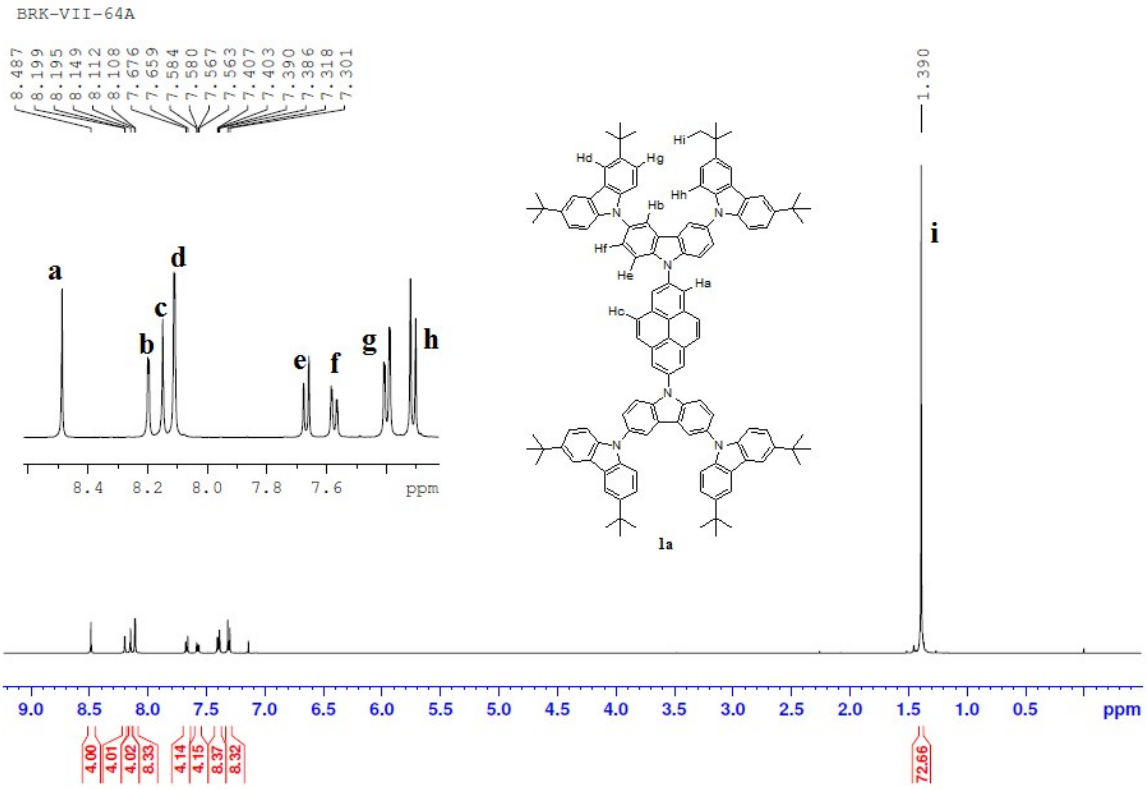


Figure S22. 500 MHz ^{1}H NMR of compound **4** in $CDCl_3$.

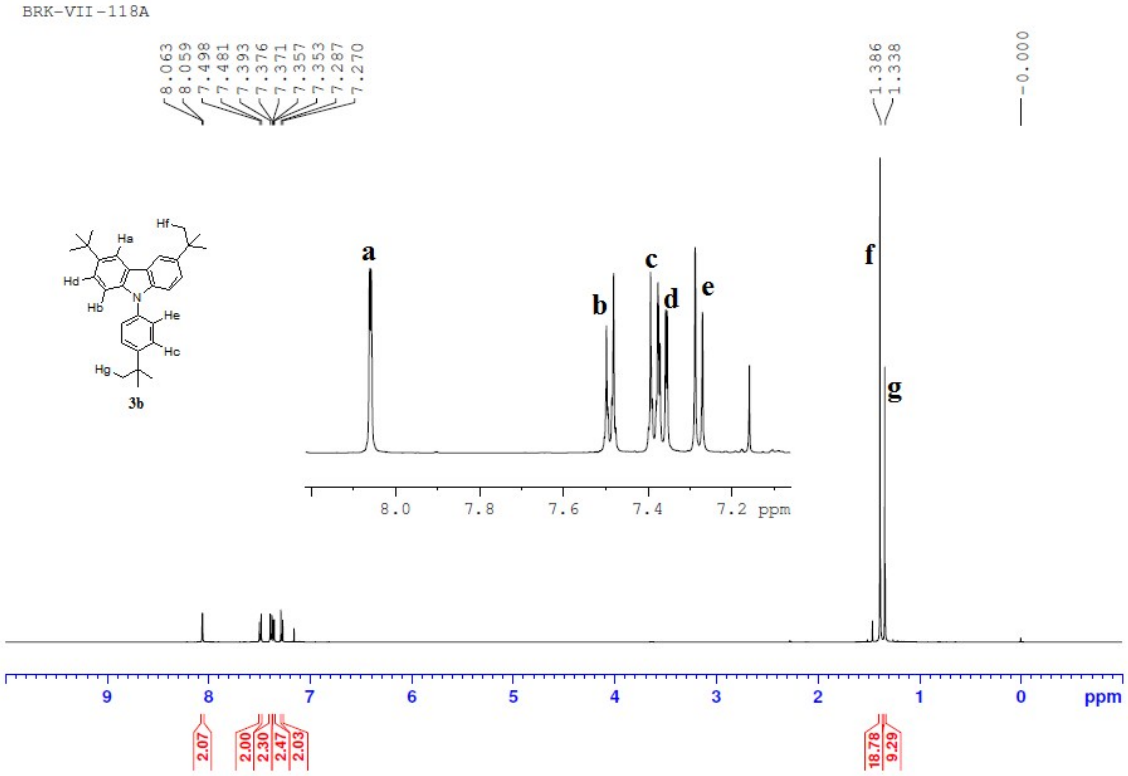


Figure S23. 500 MHz ^{1}H NMR of compound **5** in $CDCl_3$.

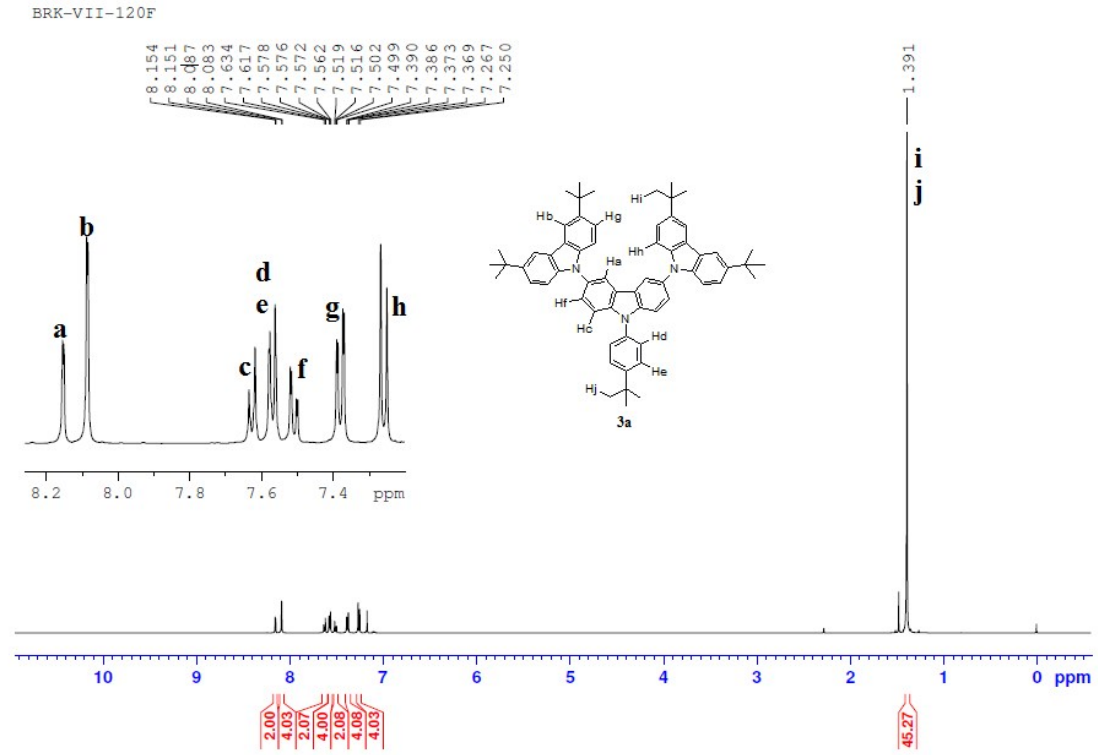


Figure S24. 500 MHz ^{1}H NMR of compound **6** in $CDCl_3$.

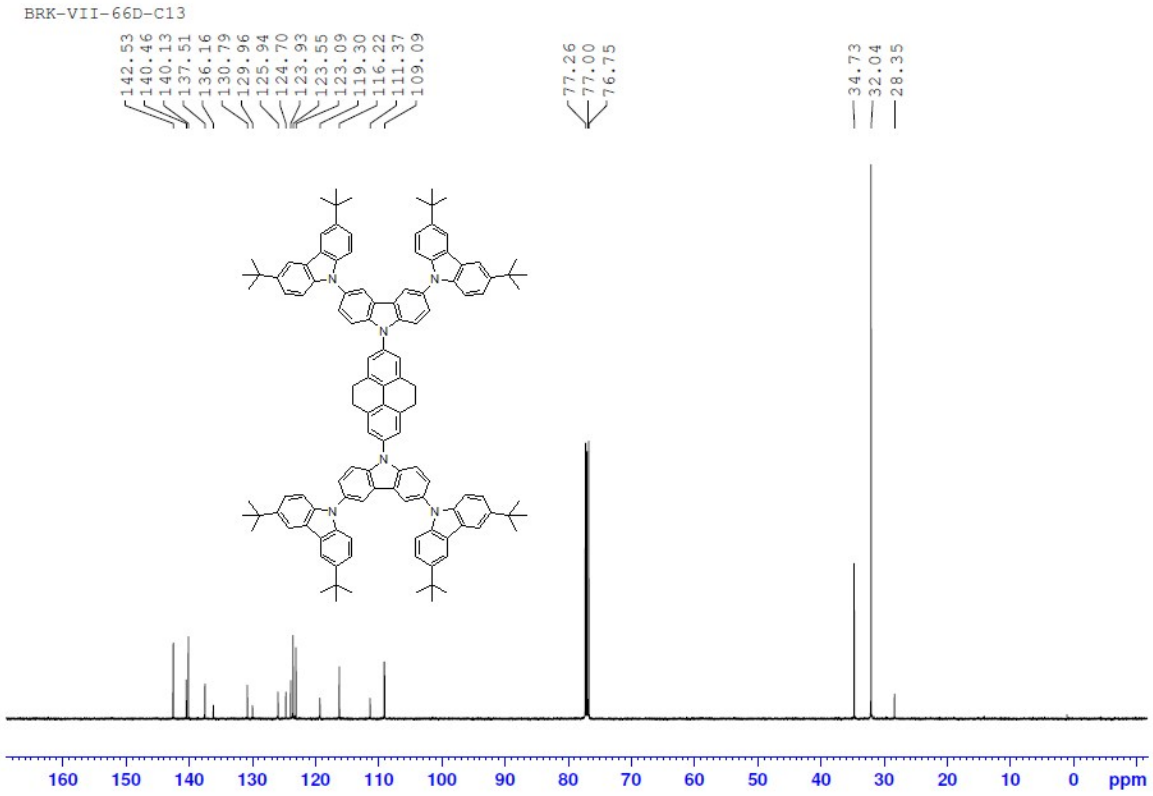


Figure S25. 125 MHz $^{13}C\{^{1}H\}$ NMR of compound **3** in $CDCl_3$.

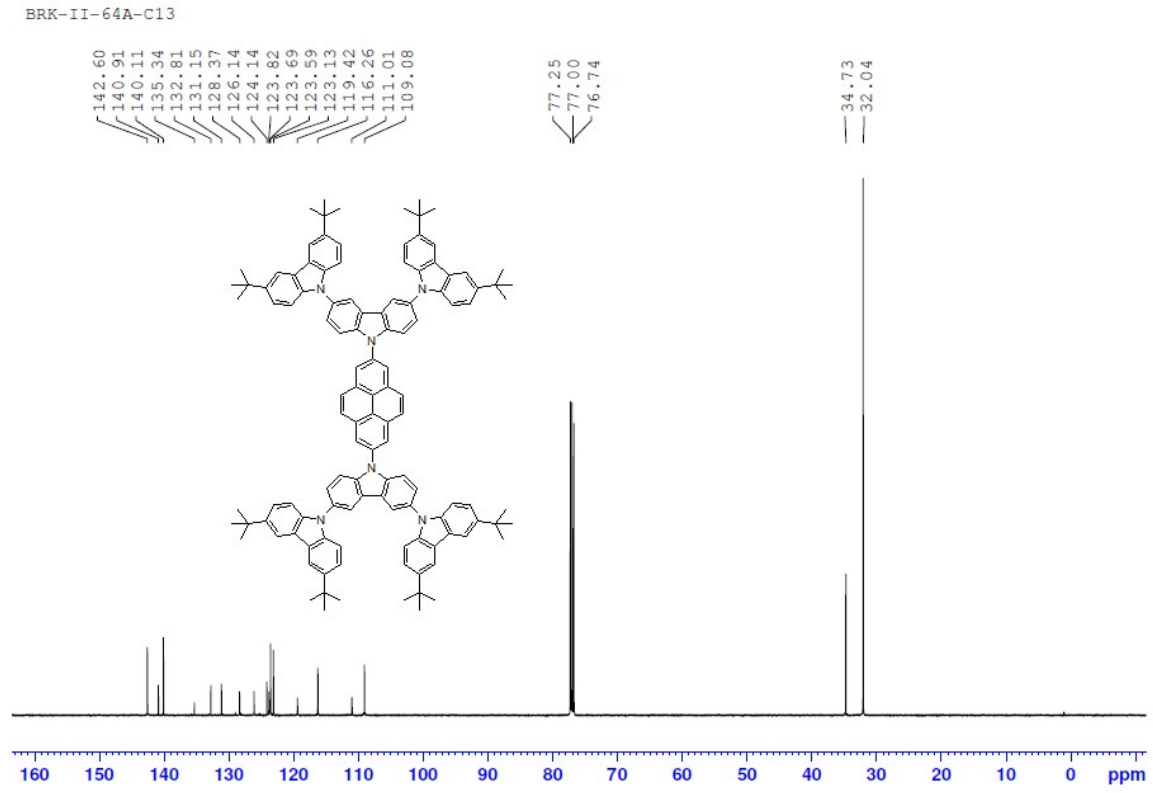


Figure S26. 125 MHz $^{13}C\{^{1}H\}$ NMR of compound **4** in $CDCl_3$.

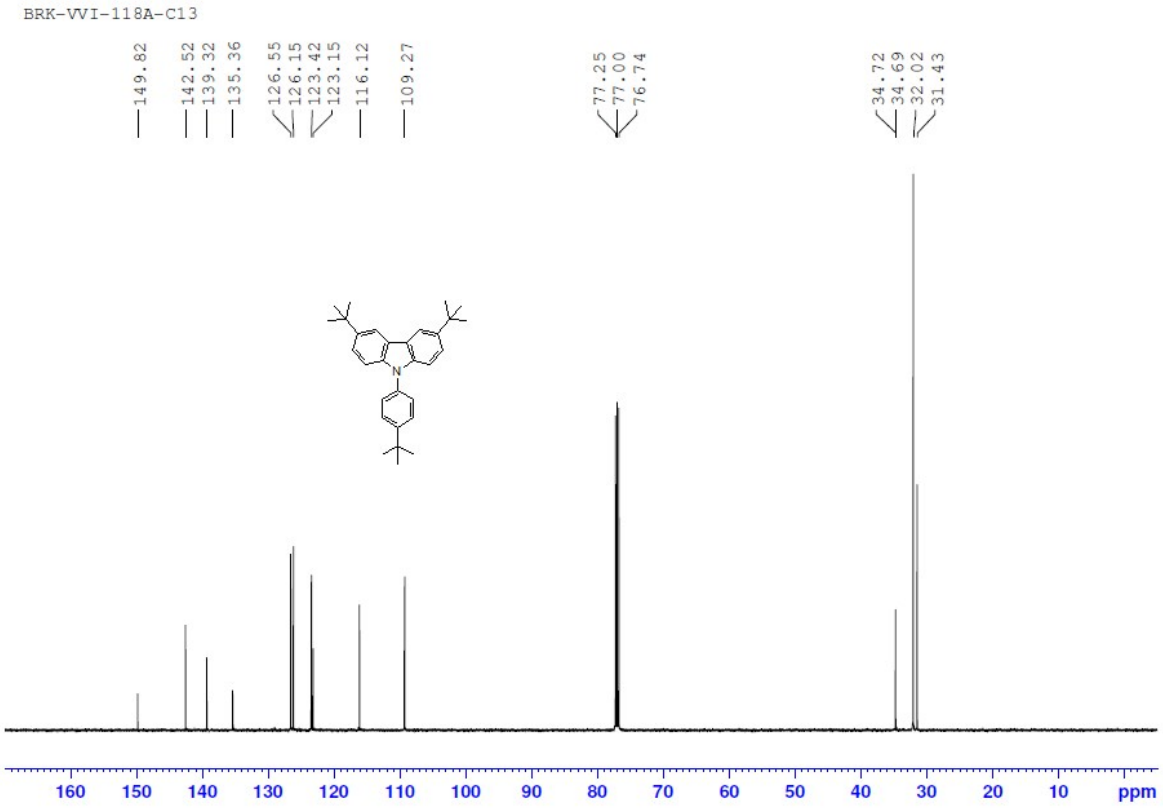


Figure S27. 125 MHz $^{13}C\{^{1}H\}$ NMR of compound **5** in $CDCl_3$.

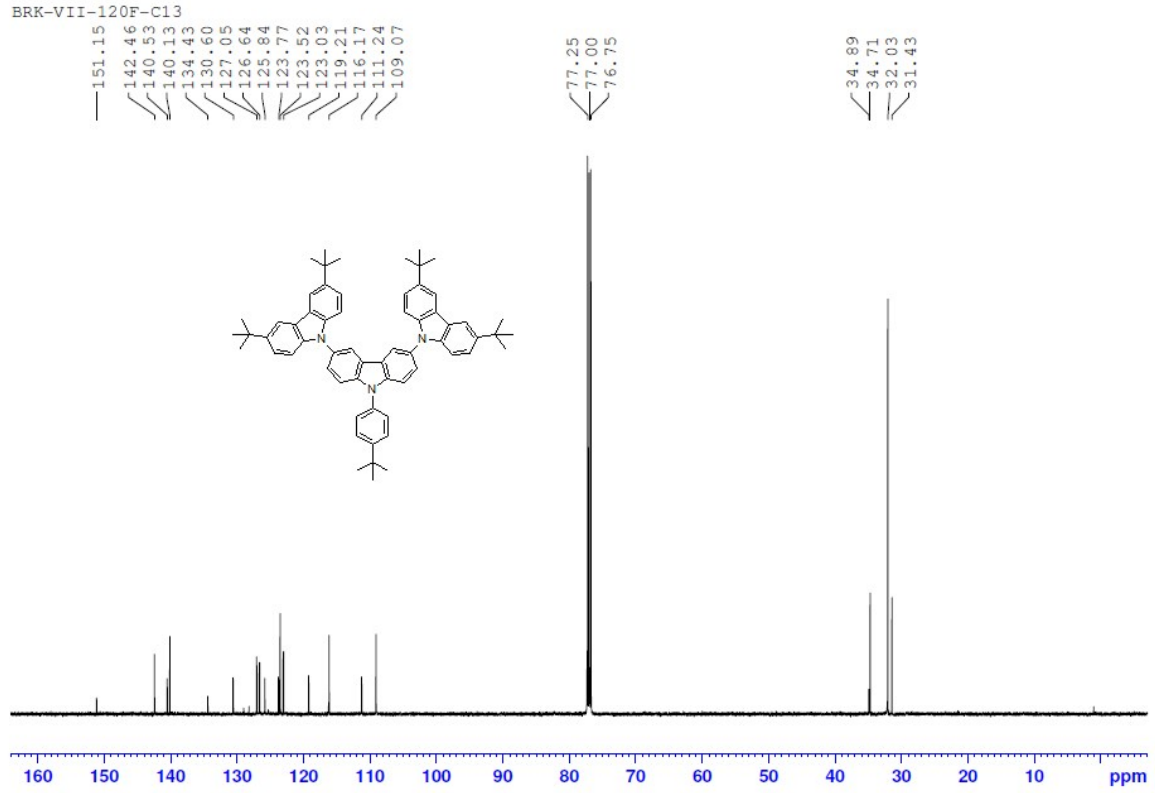


Figure S28. 125 MHz $^{13}C\{^{1}H\}$ NMR of compound **6** in $CDCl_3$.

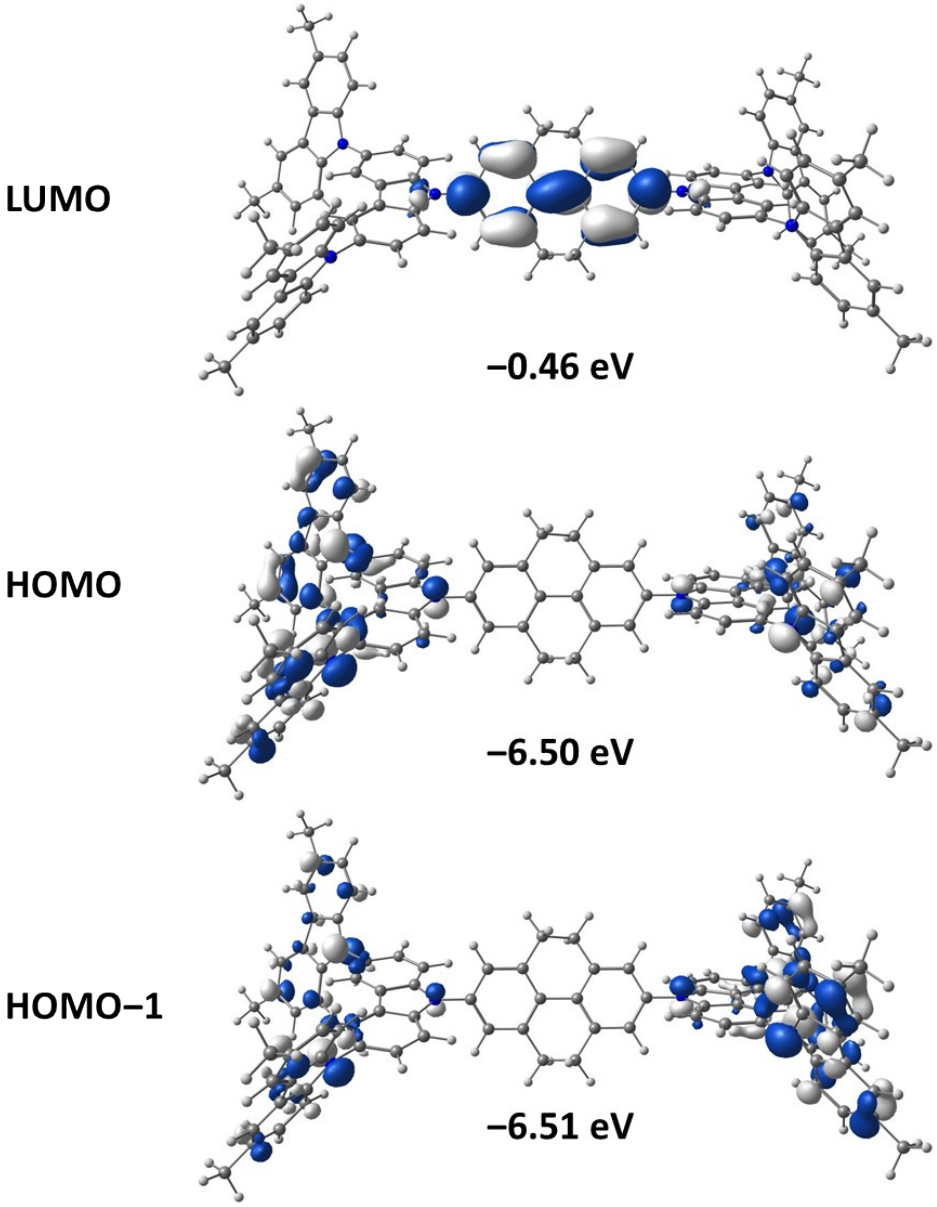


Figure S29. Pictorial representations of select frontier molecular orbitals of **3** as determined at the OT-ωB97X-D/6-31g(d,p) level of theory.

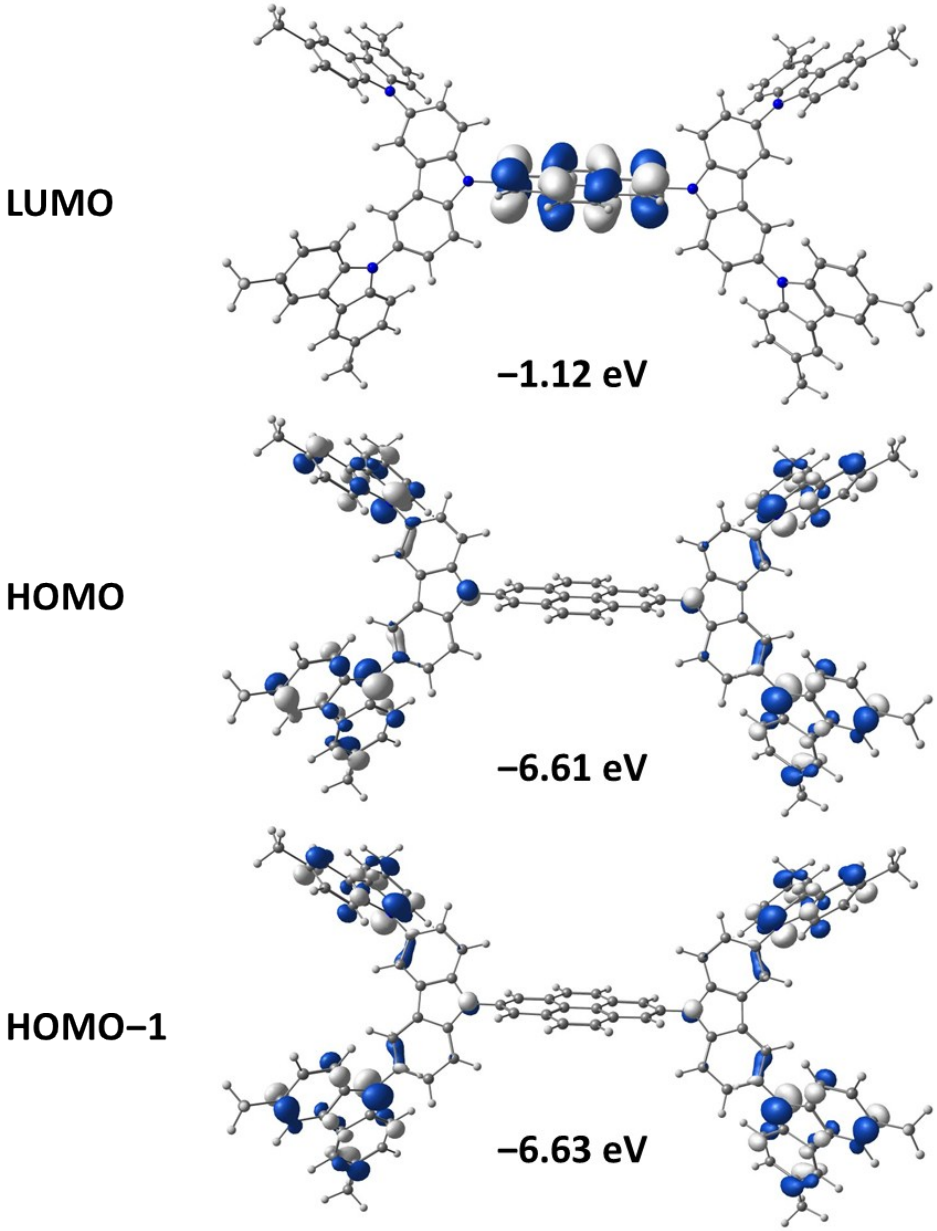


Figure S30. Pictorial representations of select frontier molecular orbitals of **4** as determined at the OT-ωB97X-D/6-31g(d,p) level of theory.

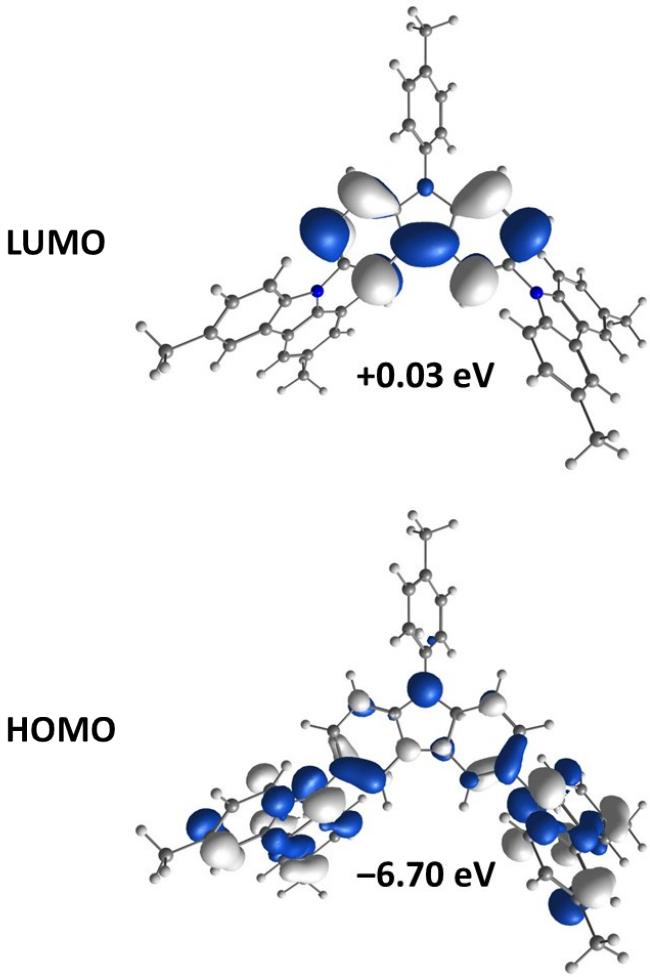


Figure S31. Pictorial representations of select frontier molecular orbitals of **6** as determined at the OT-ωB97X-D/6-31g(d,p) level of theory.

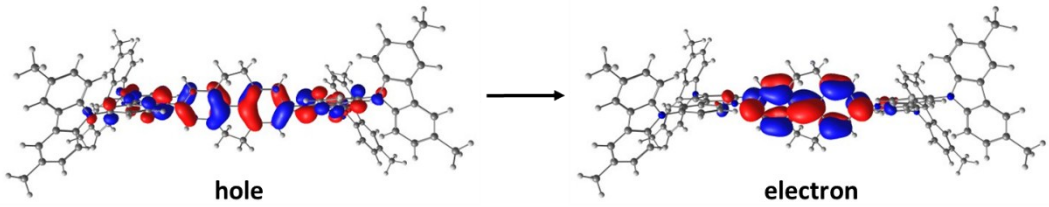


Figure S32. Pictorial representations of the natural transition orbitals (NTO) for the $S_0 \rightarrow S_3$ transition of **3** as determined at the TD-OT-ωB97X-D/6-31g(d,p) level of theory.

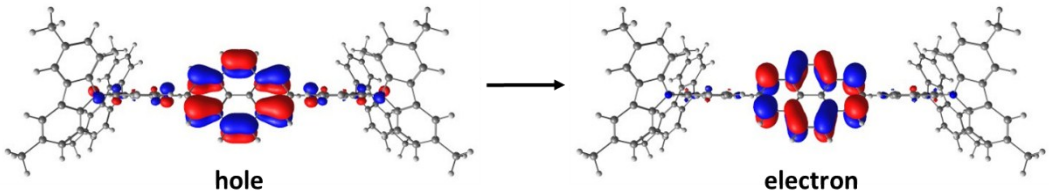


Figure S33. Pictorial representations of the natural transition orbitals (NTO) for the $S_0 \rightarrow S_3$ transition of **4** as determined at the TD-OT-ωB97X-D/6-31g(d,p) level of theory.

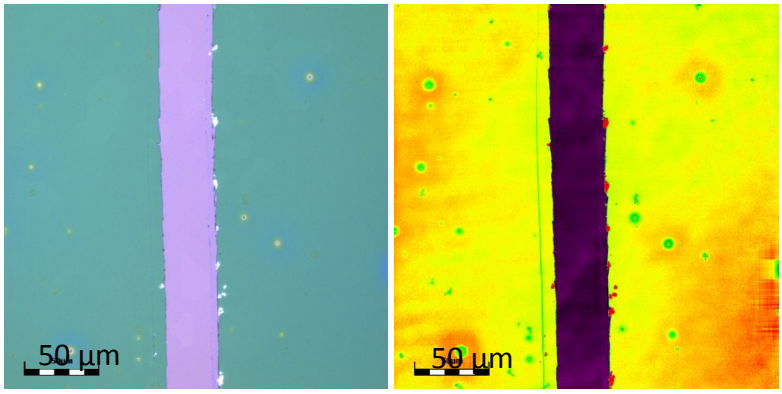


Figure S34. Laser scanning microscope images of thin film of compound **3** (color, left; height, right), showing good overall film formation quality, with no visible cracks or inhomogeneities. The large feature in the middle of each image is a result of a scratch made in the film to measure its thickness.

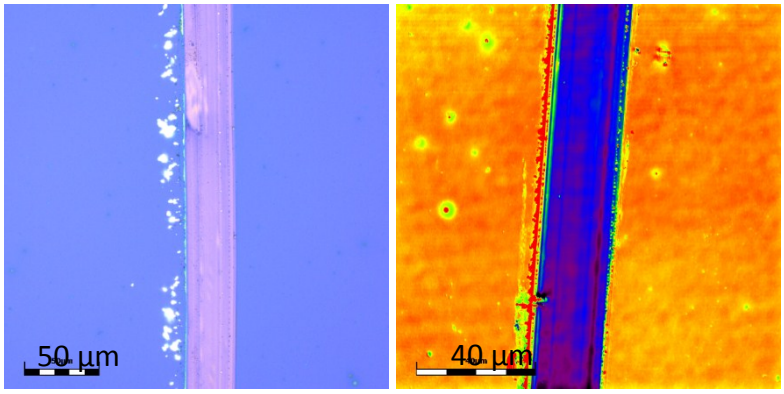


Figure S35. Laser scanning microscope images of thin film of compound **4** (color, left; height, right), showing good overall film formation quality, with no visible cracks or inhomogeneities. The large feature in the middle of each image is a result of a scratch made in the film to measure its thickness.

Reference

1. K. Dimroth, C. Reichardt, T. Siepmann and F. Bohlmann *Ann.* 1963, **661**, 1-37.