Electronic Supporting Information

Tetraaryl Pyrenes: Photophysical Properties, Computational Studies, Crystal Structures, and Application in OLEDs

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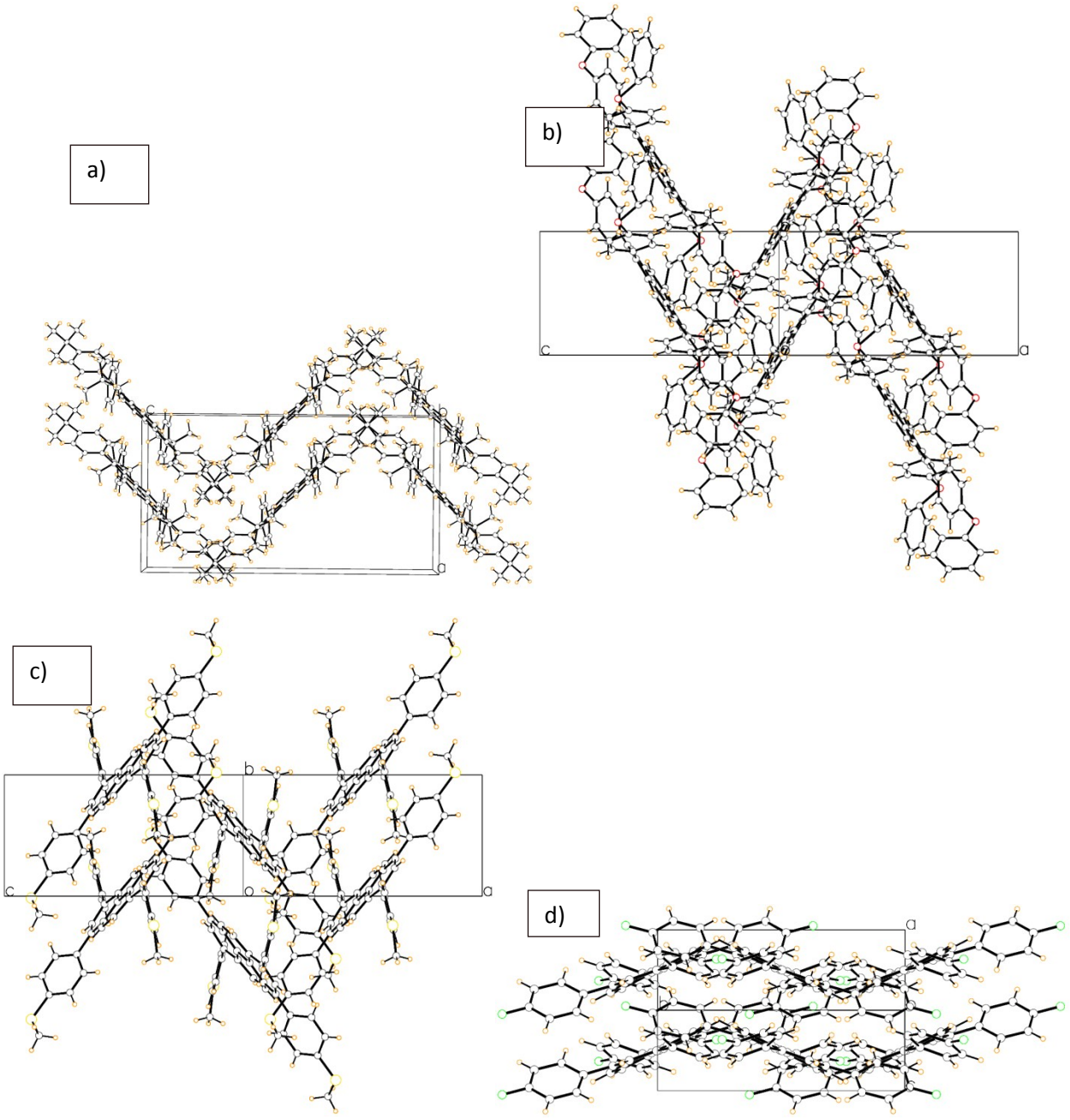

a)
b)
c)
d)

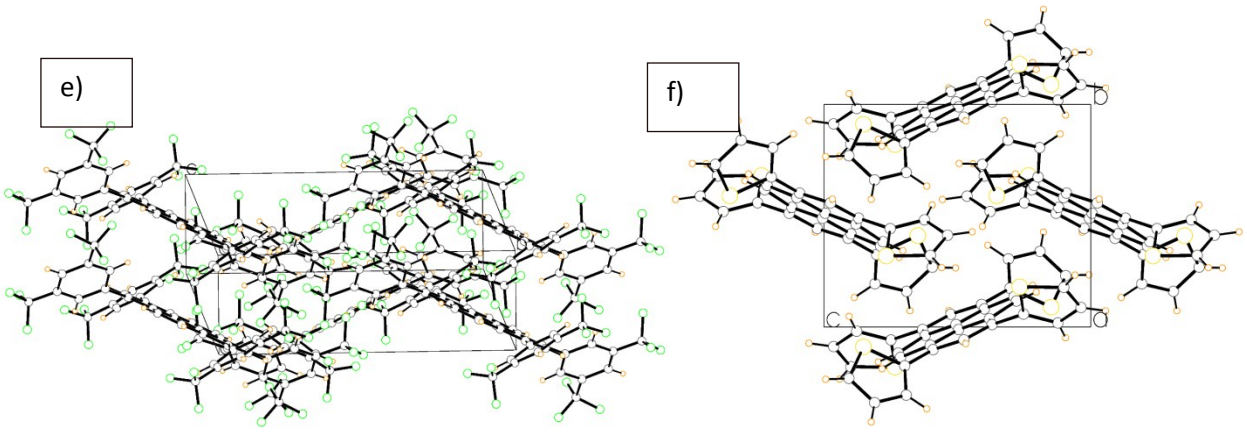


Figure S1. Crystal packing of compounds a) **1**, b) **2**, c) **4**, d) **5**, e) **7**, and f) **9**.

NMR

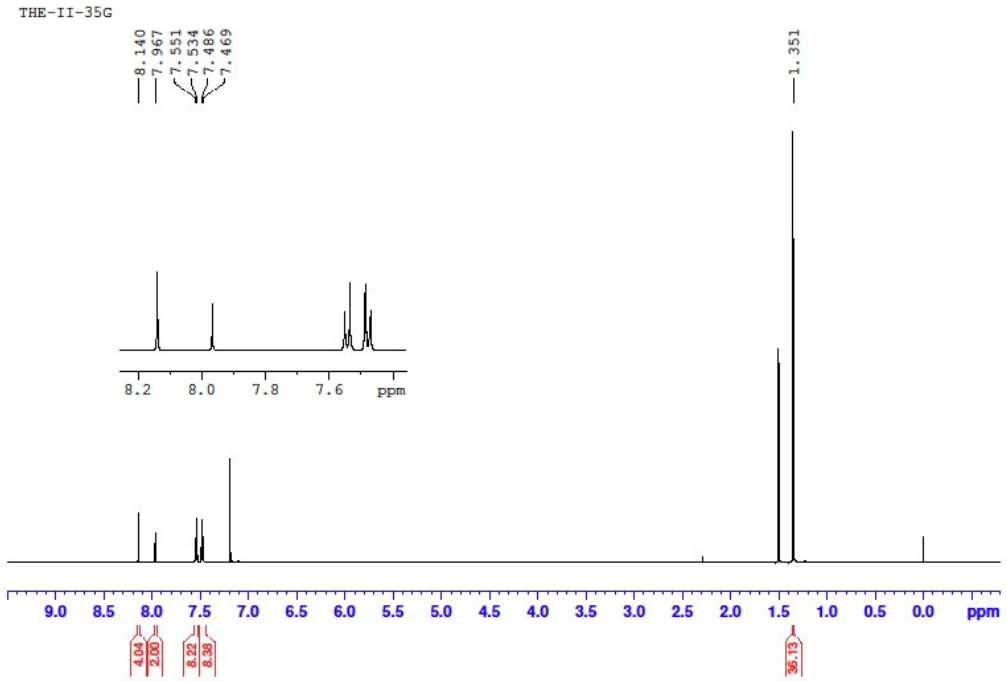


Figure S2. ^{1}H NMR of 1,3,6,8-tetrakis(4-(*tert*-butyl)phenyl)pyrene **(1)** in $CDCl_3$.

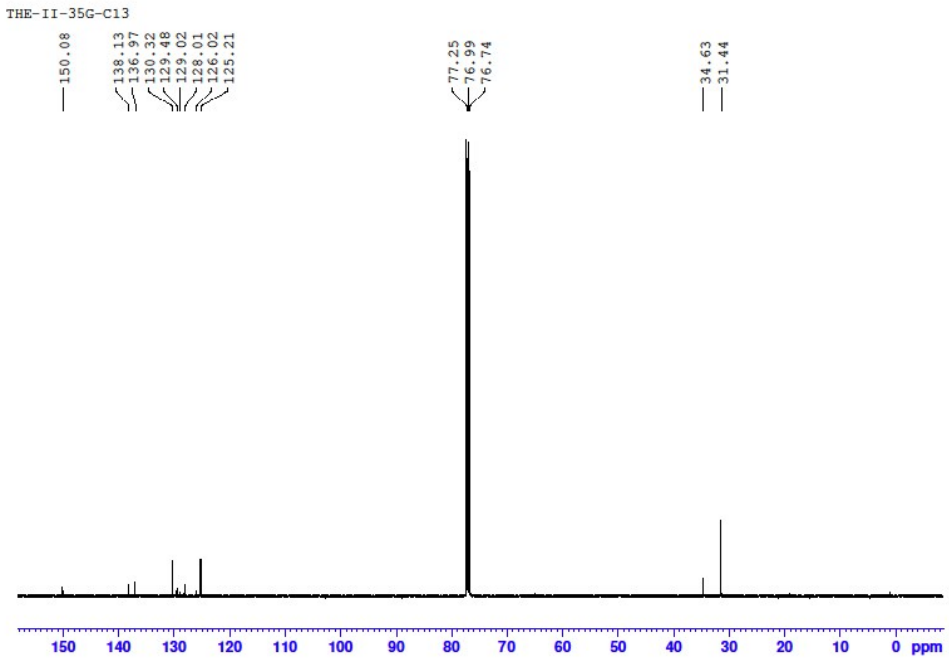


Figure S3. ^{13}C NMR of 1,3,6,8-tetrakis(4-(*tert*-butyl)phenyl)pyrene **(1)** in $CDCl_3$.

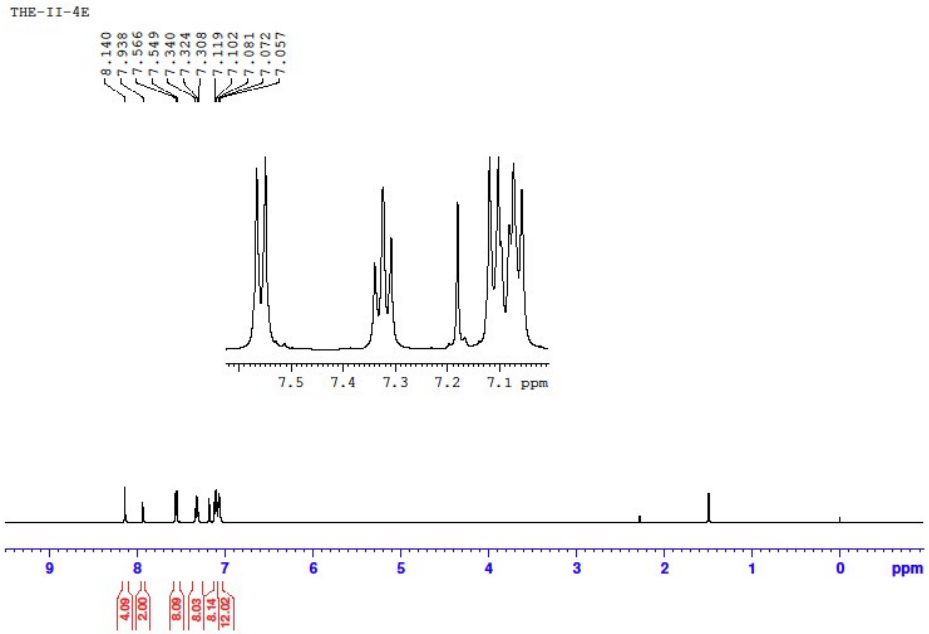


Figure S4. ^{1}H NMR of 1,3,6,8-tetrakis(4-phenoxyphenyl)pyrene (**2**) in $CDCl_3$.

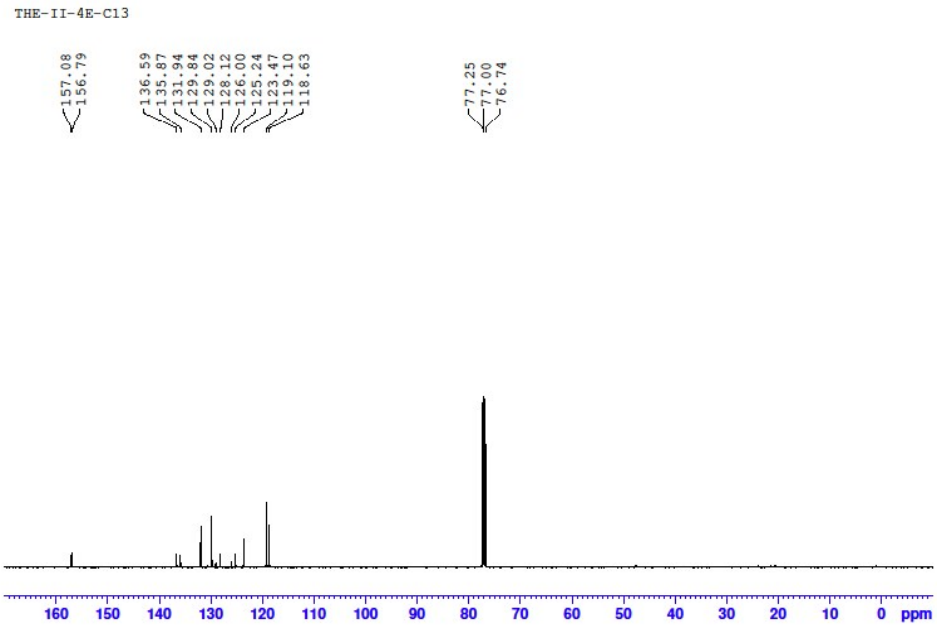


Figure S5. ^{13}C NMR of 1,3,6,8-tetrakis(4-phenoxyphenyl)pyrene (**2**) in $CDCl_3$.

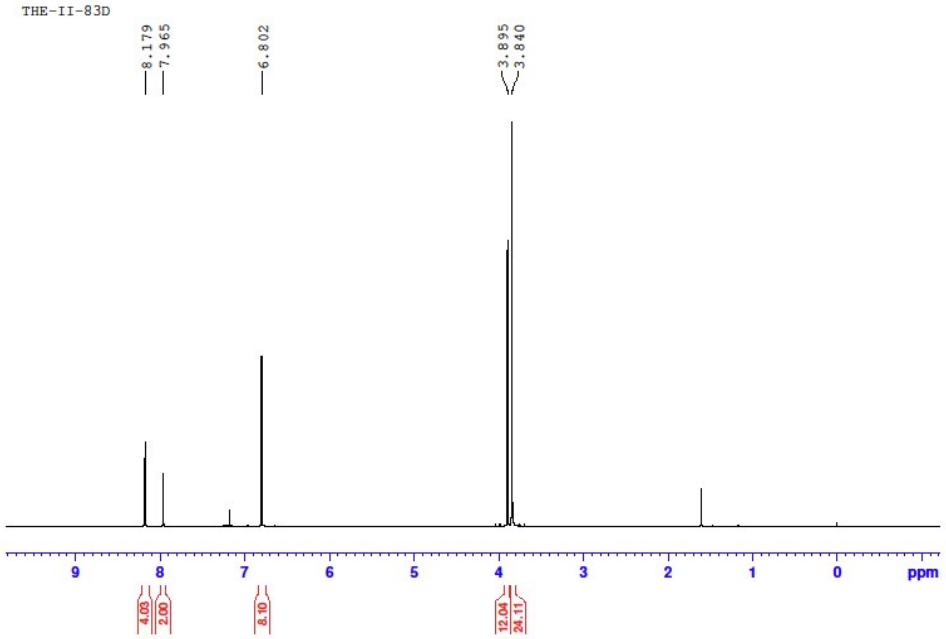


Figure S6. ^{1}H NMR of 1,3,6,8-tetrakis(3,4,5-trimethoxyphenyl)pyrene (**3**) in $CDCl_3$.

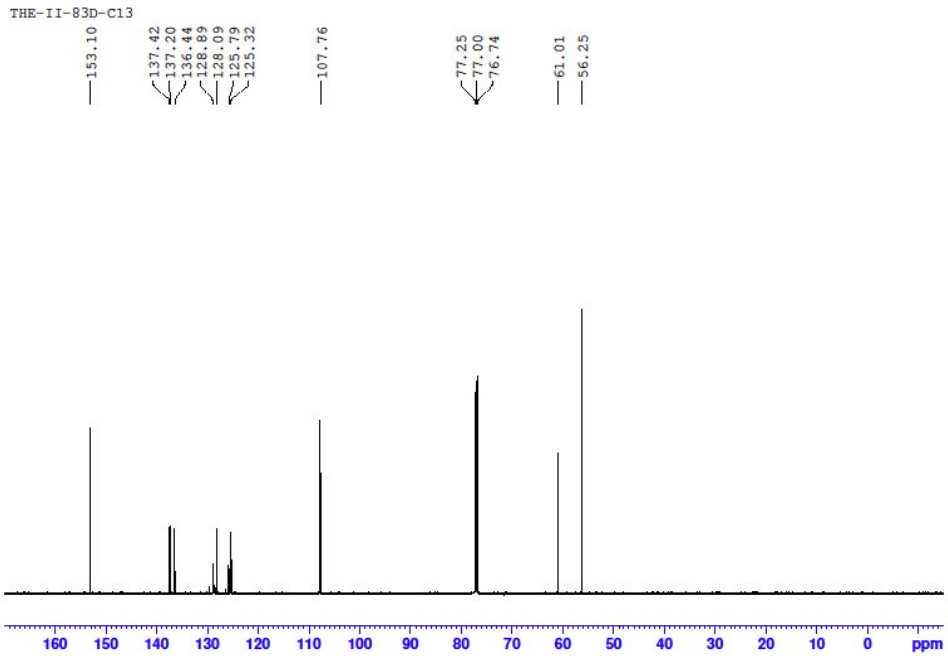


Figure S7. ^{13}C NMR of 1,3,6,8-tetrakis(3,4,5-trimethoxyphenyl)pyrene (**3**) in $CDCl_3$.

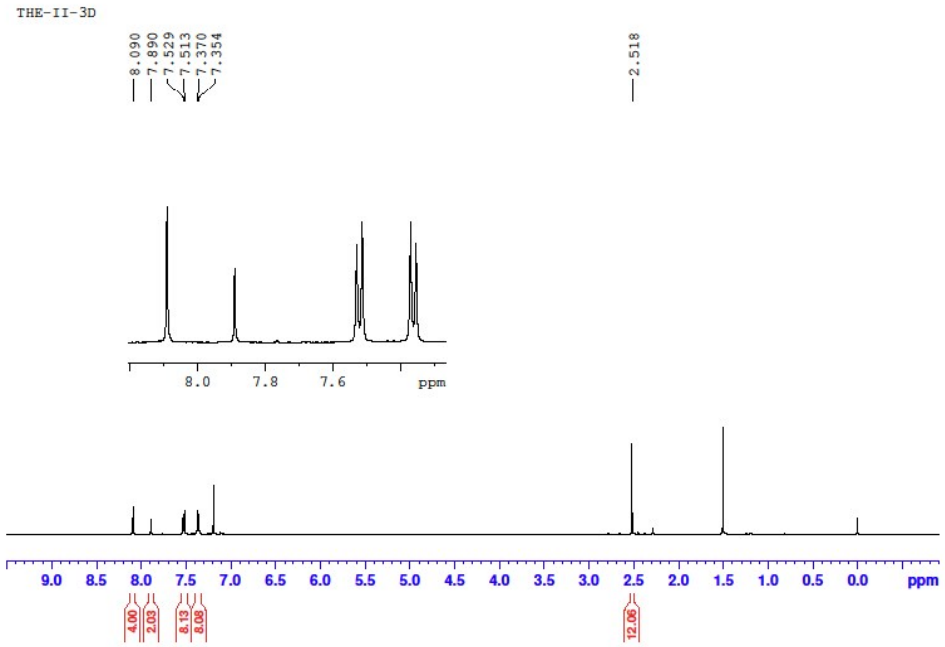


Figure S8. ^{1}H NMR of 1,3,6,8-tetrakis(4-(methylthio)phenyl)pyrene (**4**) in $CDCl_3$.

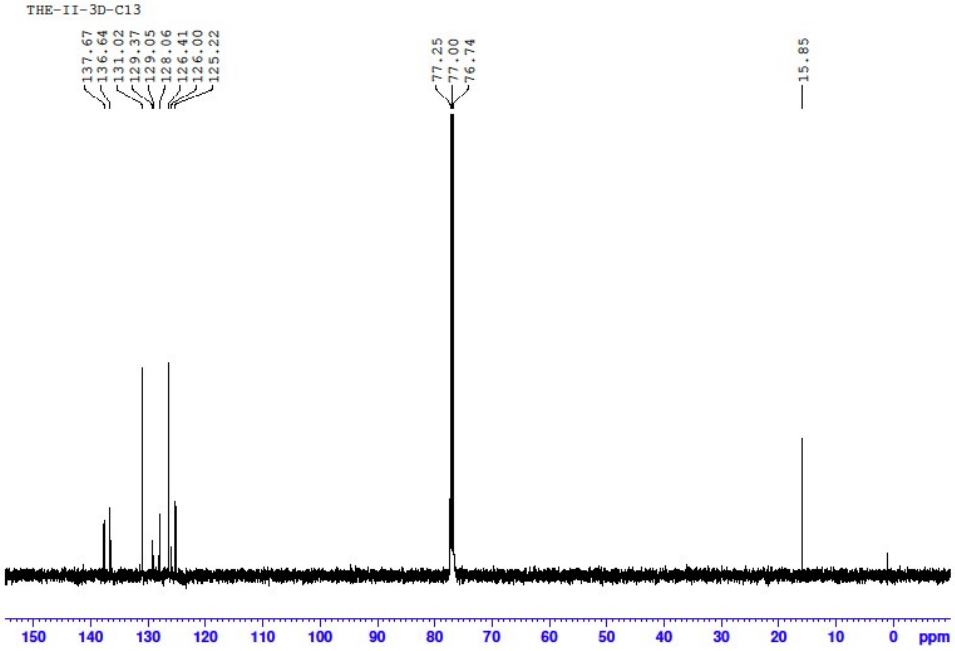


Figure S9. ^{13}C NMR of 1,3,6,8-tetrakis(4-(methylthio)phenyl)pyrene (**4**) in $CDCl_3$.

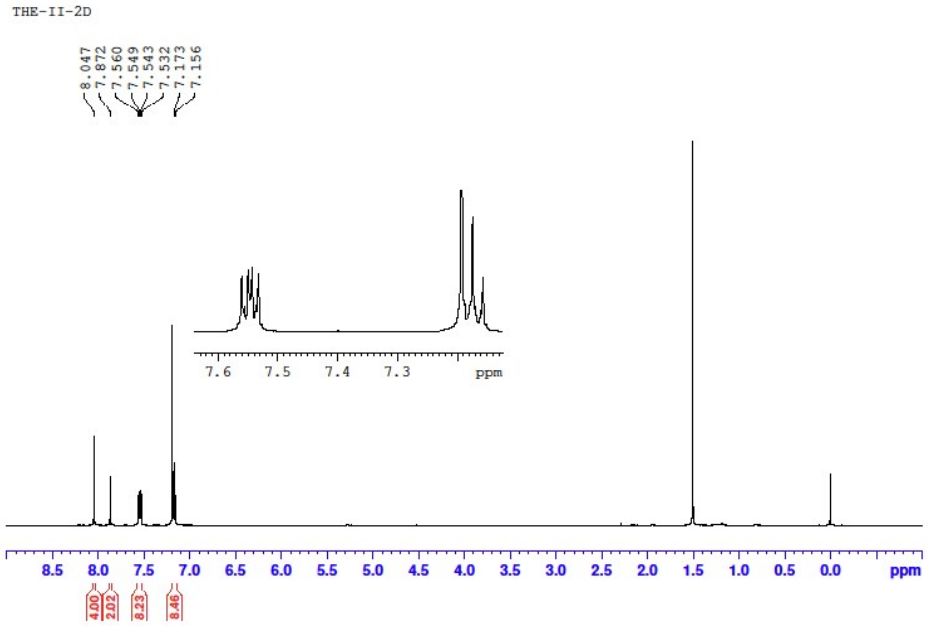


Figure S10. ^{1}H NMR of 1,3,6,8-tetrakis(4-fluorophenyl)pyrene (**5**) in $CDCl_3$.

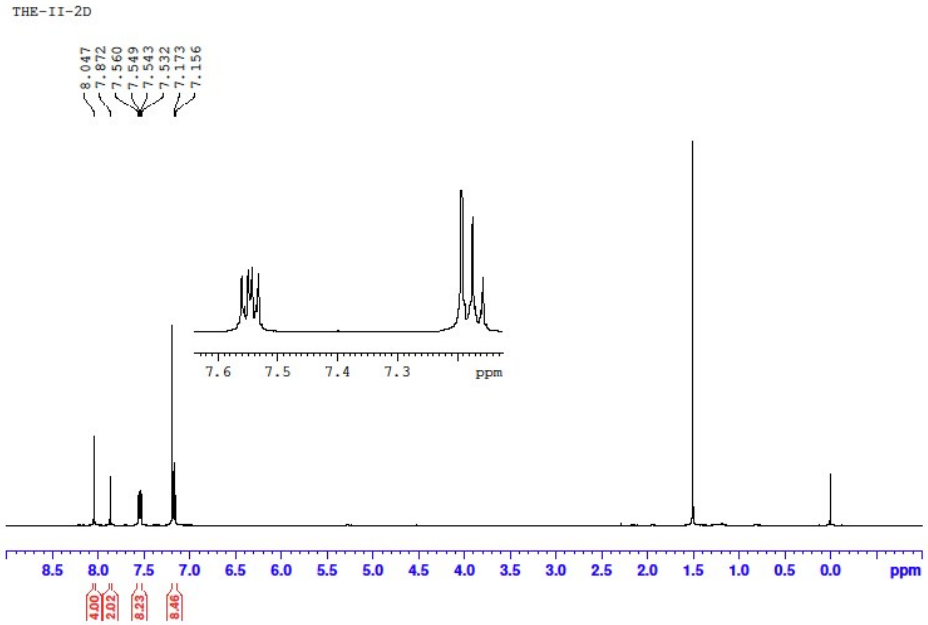


Figure S11. ^{13}C NMR of 1,3,6,8-tetrakis(4-fluorophenyl)pyrene (**5**) in $CDCl_3$.

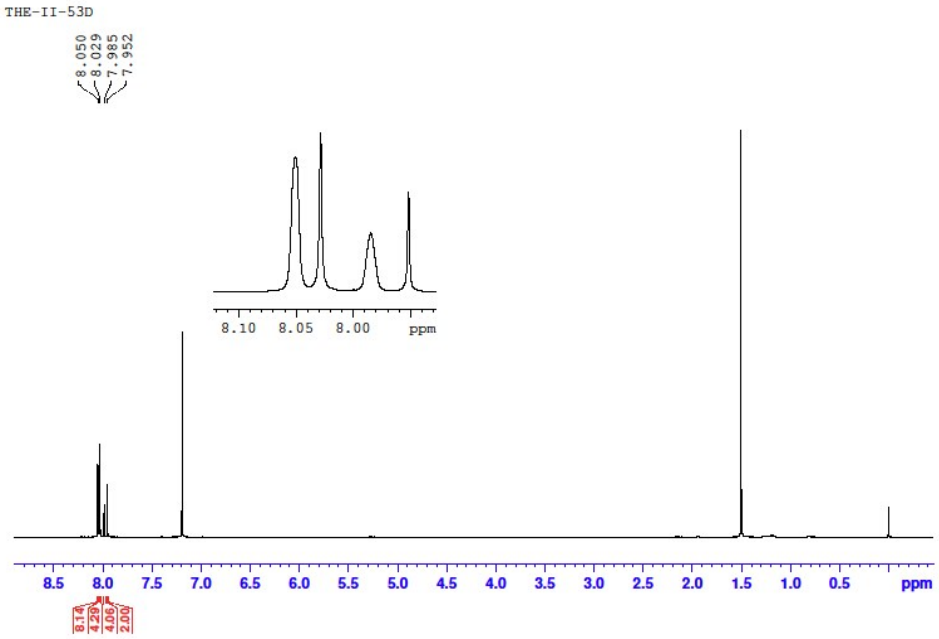


Figure S12. ^{1}H NMR of 1,3,6,8-tetrakis(3,5-bis(trifluoromethyl)phenyl)pyrene (**7**) in $CDCl_3$.

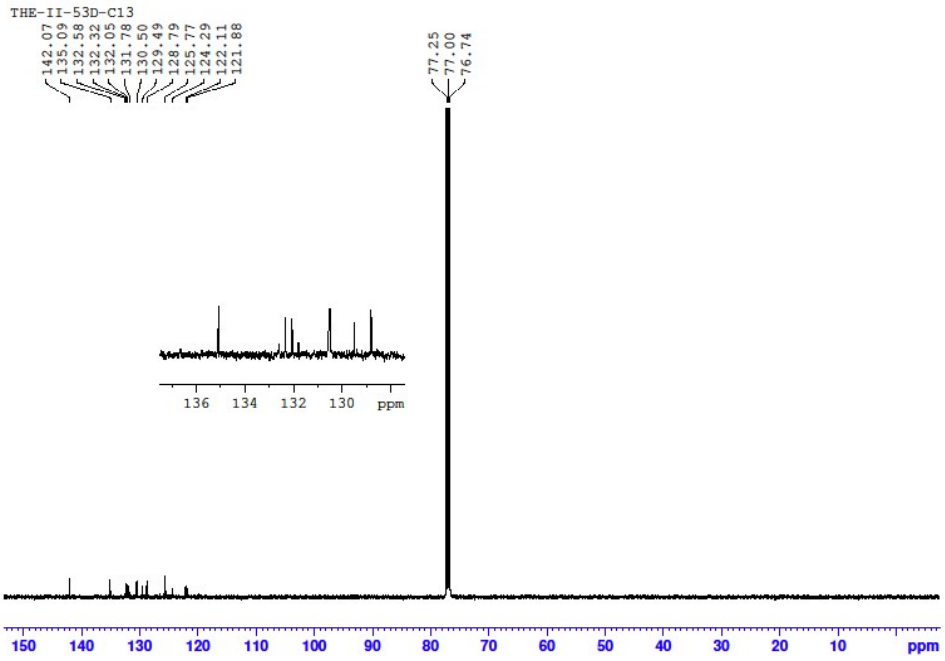


Figure S13. ^{13}C NMR of 1,3,6,8-tetrakis(3,5-bis(trifluoromethyl)phenyl)pyrene (**7**) in $CDCl_3$.

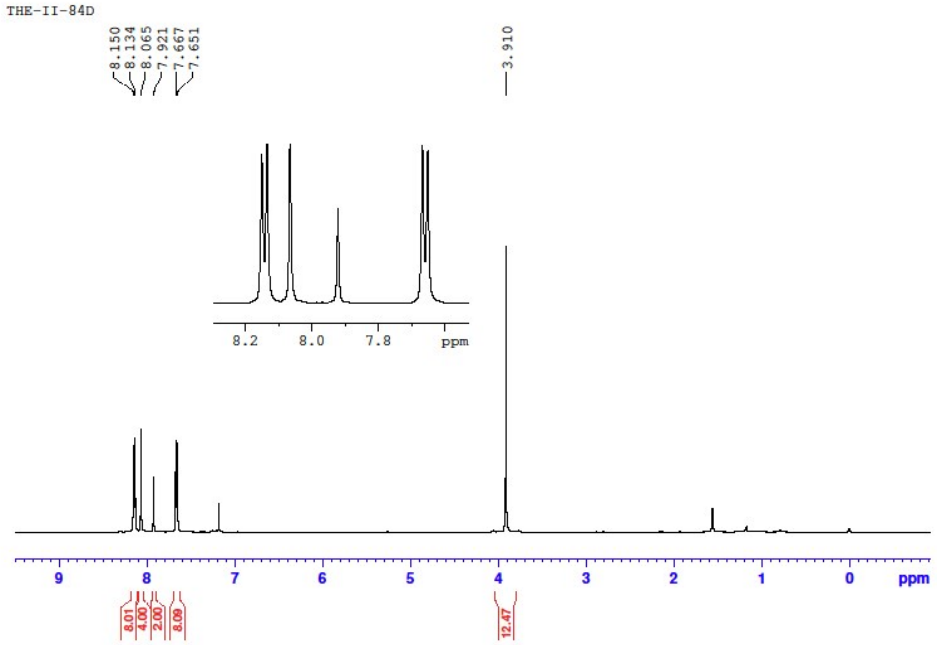


Figure S14. ^{1}H NMR of tetramethyl 4,4',4",4"'-(pyrene-1,3,6,8-tetrayl)tetrabenzoate (8) at in $CDCl_3$.

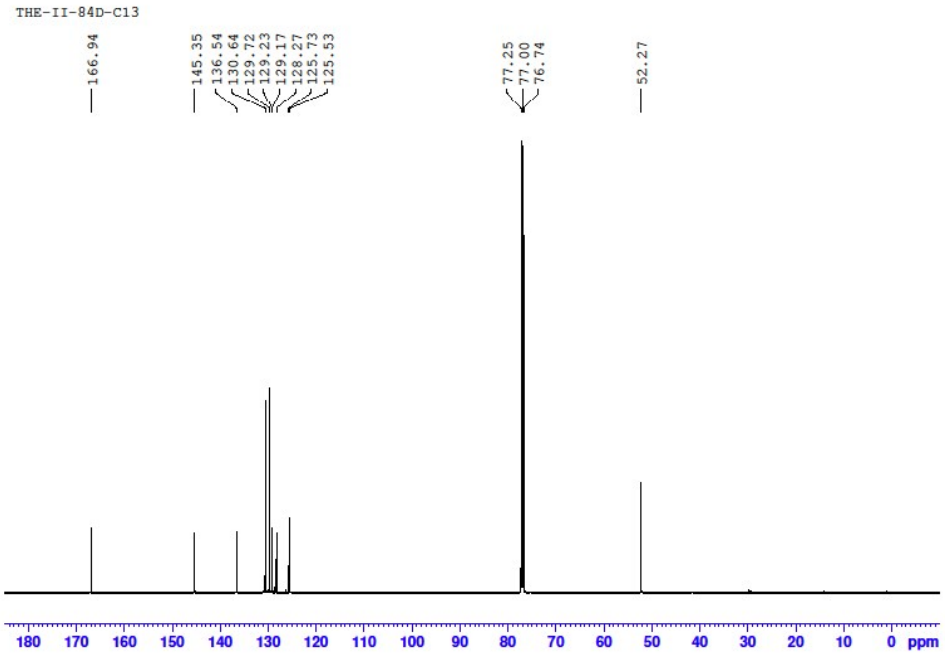


Figure S15. ^{13}C NMR of tetramethyl 4,4',4",4"'-(pyrene-1,3,6,8-tetrayl)tetrabenzoate (**8**) in $CDCl_3$.

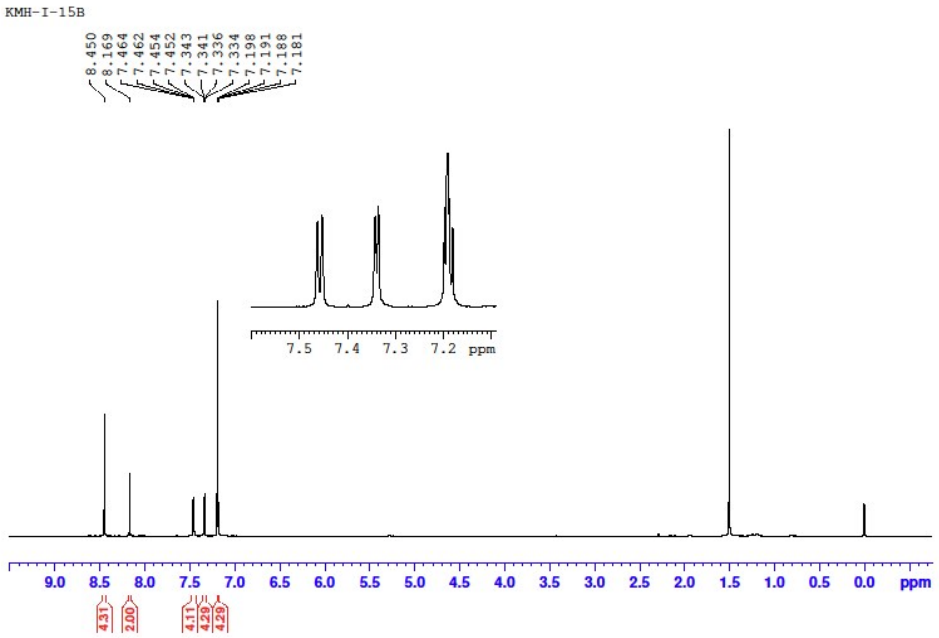


Figure S16. ^{1}H NMR of 1,3,6,8-tetrakis(thiophen-2-yl)pyrene (**9**) in $CDCl_3$.

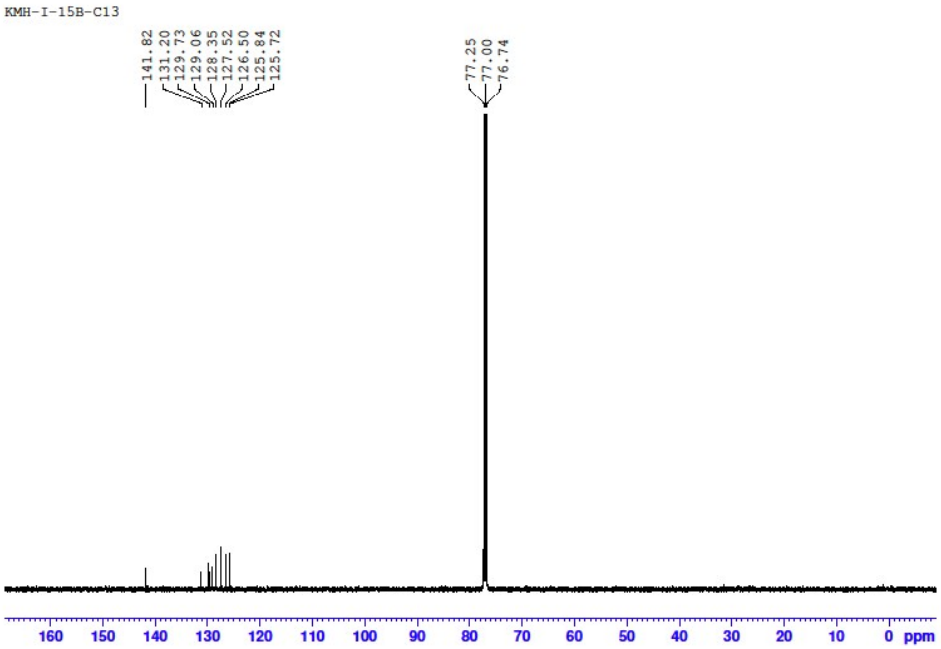


Figure S17. ^{13}C NMR of 1,3,6,8-tetrakis(thiophen-2-yl)pyrene (**9**) in $CDCl_3$.

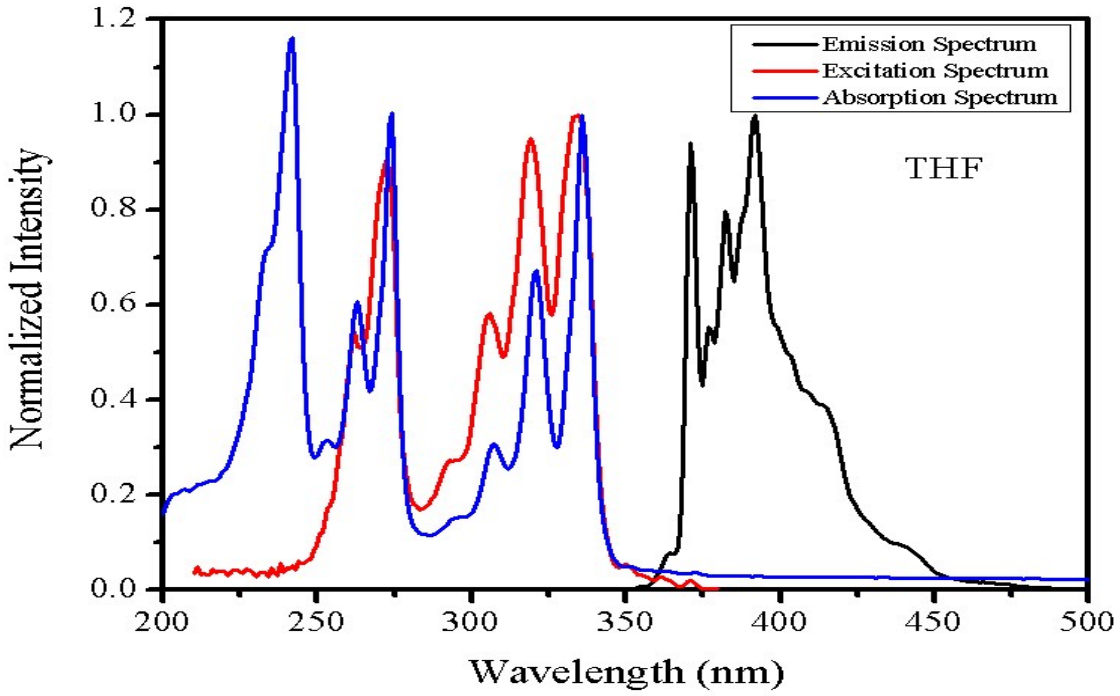


Figure S18. Normalized absorption, excitation and emission spectrum of **pyrene** in tetrahydrofuran.

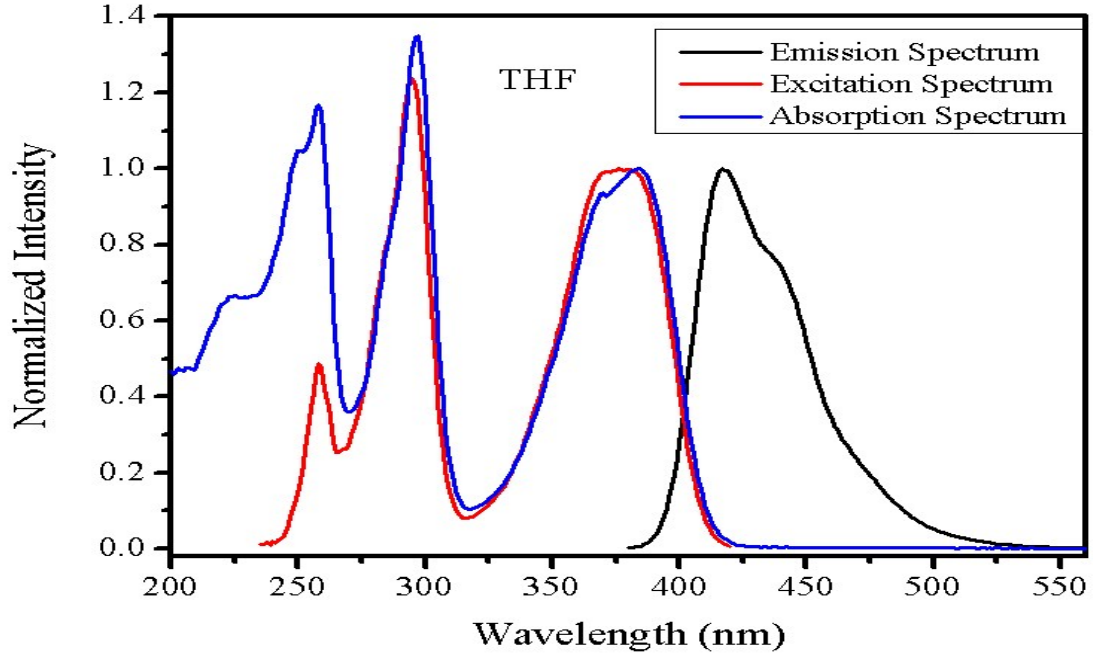


Figure S19. Normalized absorption, excitation and emission spectrum of **1,3,6,8-tetraphenylpyrene (TPP)** in tetrahydrofuran.

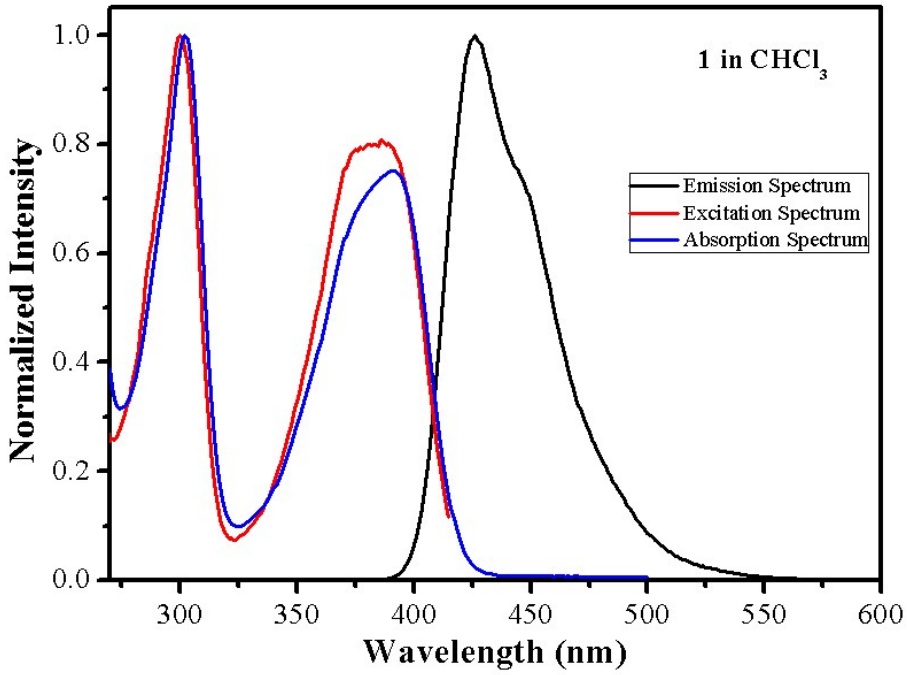


Figure S20. Normalized absorption, excitation and emission spectrum of **1** in chloroform.

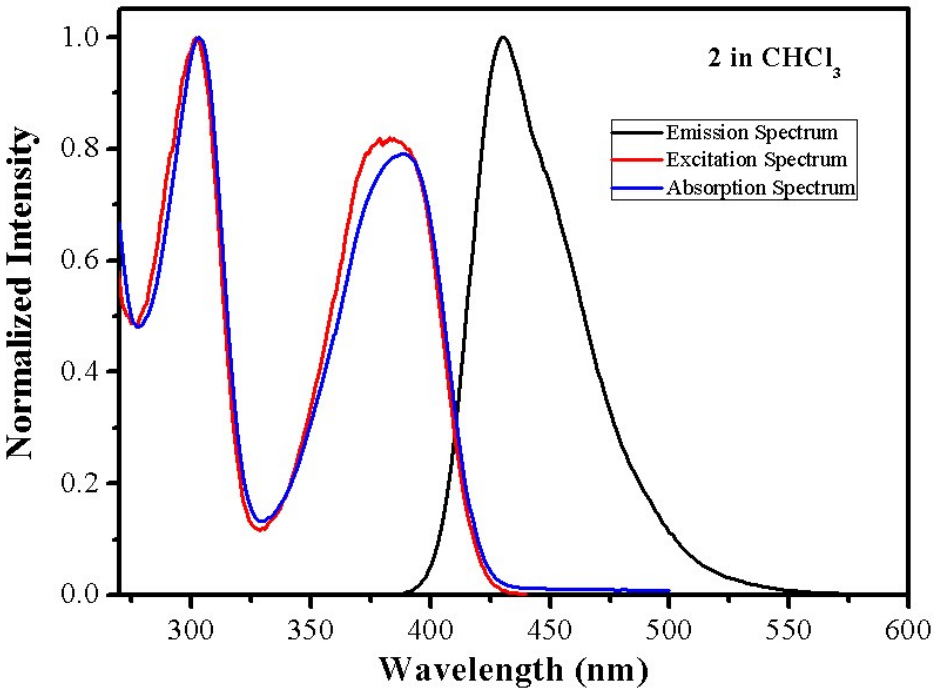


Figure S21. Normalized absorption, excitation and emission spectrum of **2** in chloroform.

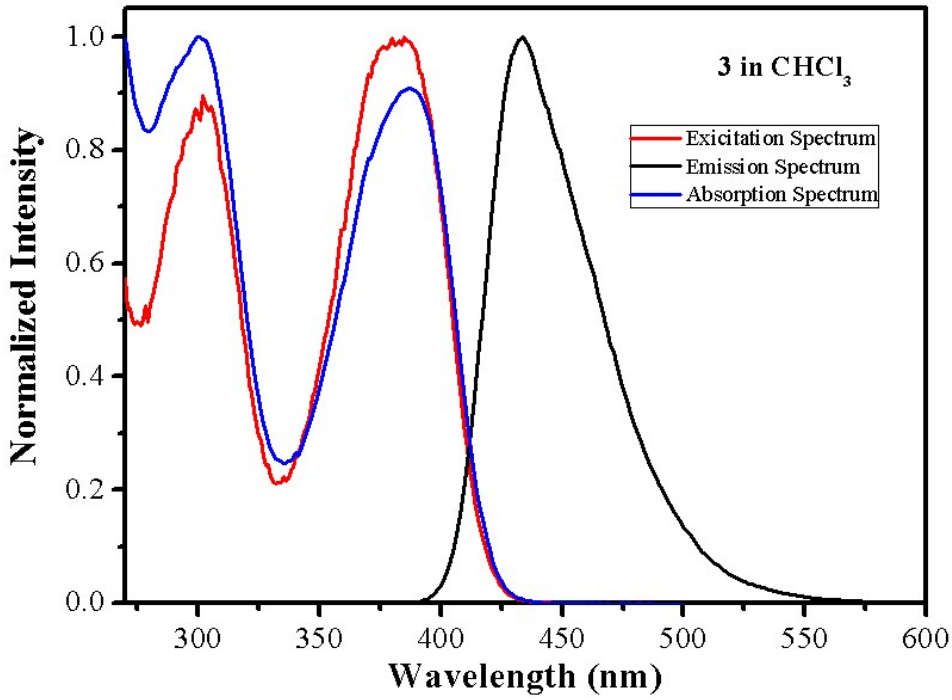


Figure S22. Normalized absorption, excitation and emission spectrum of **3** in chloroform

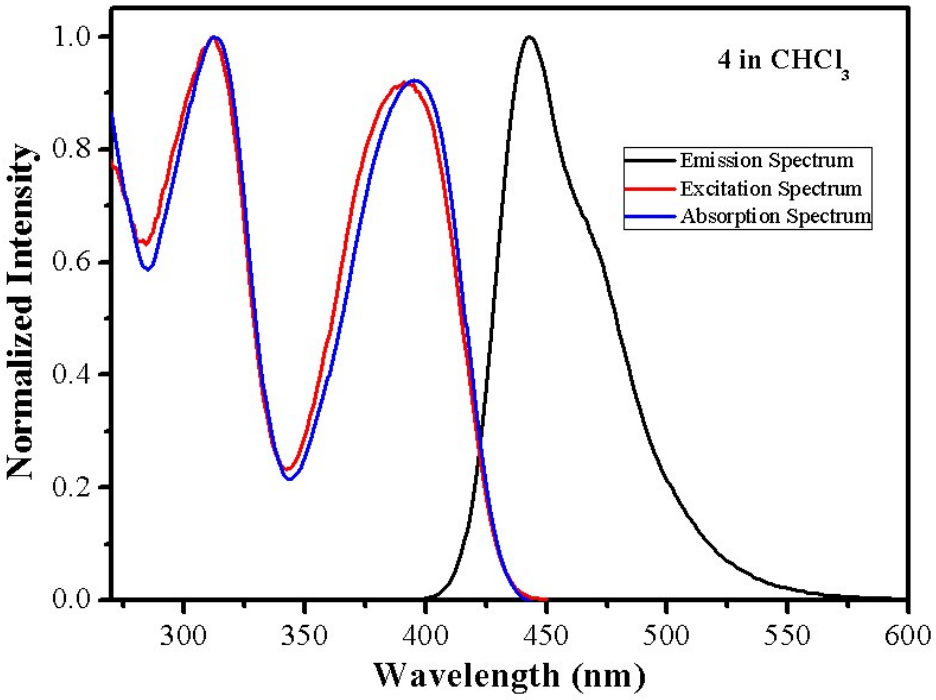


Figure S23. Normalized absorption, excitation and emission spectrum of **4** in chloroform.

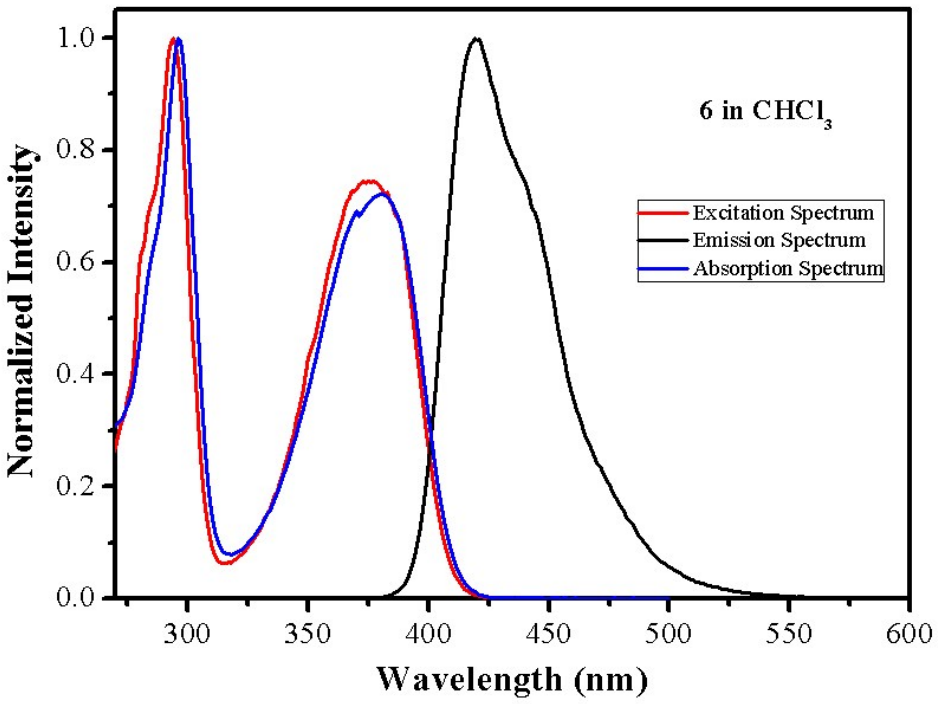


Figure S24. Normalized absorption, excitation and emission spectrum of **6** in chloroform

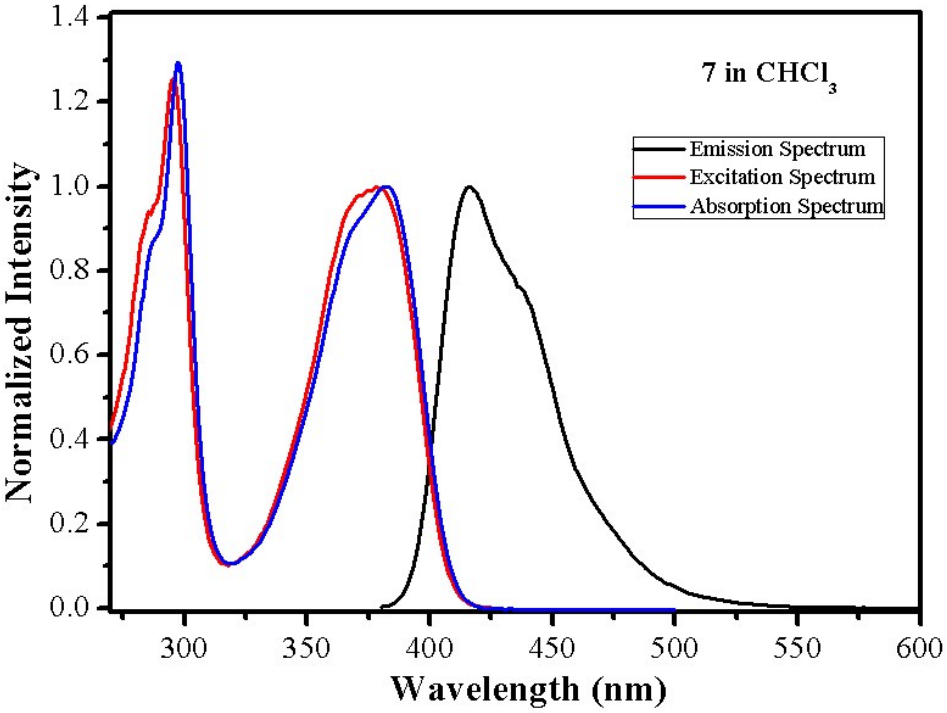


Figure S25. Normalized absorption, excitation and emission spectrum of **7** in chloroform.

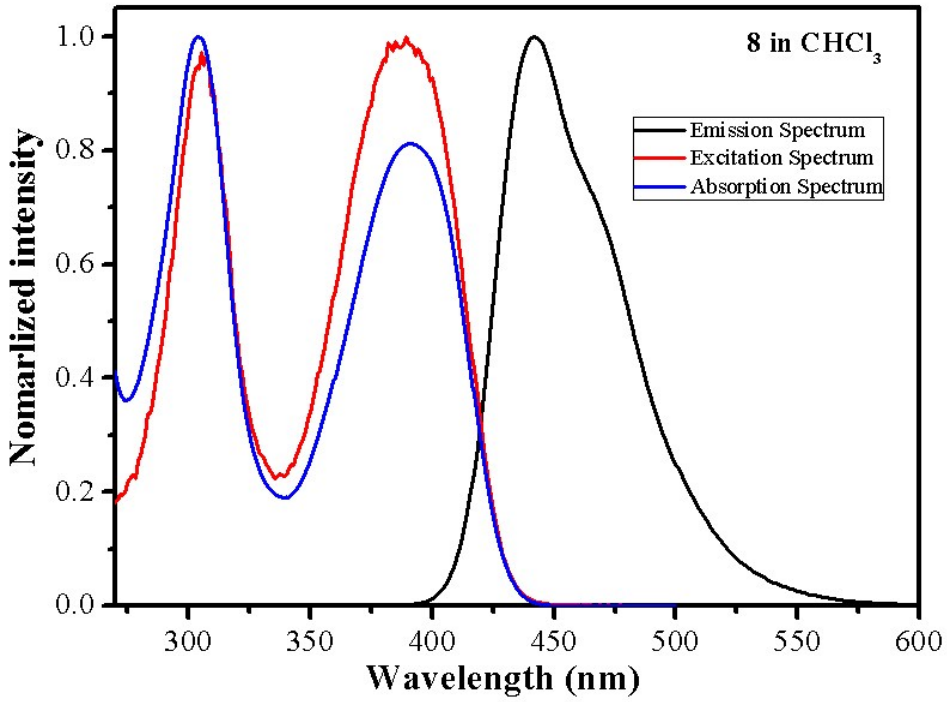


Figure S26. Normalized absorption, excitation and emission spectrum of **8** in chloroform.

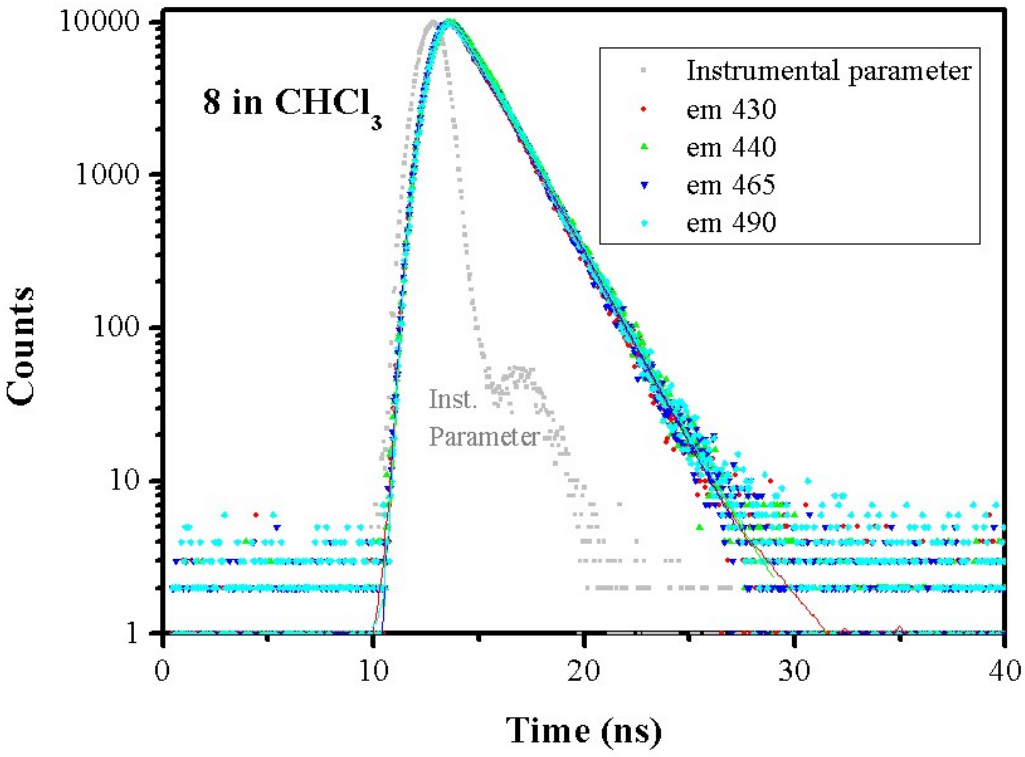


Figure S27. Fluorescence lifetime profile at various possible emission wavelengths keep the excitation wavelength constant in chloroform for compound **8**.

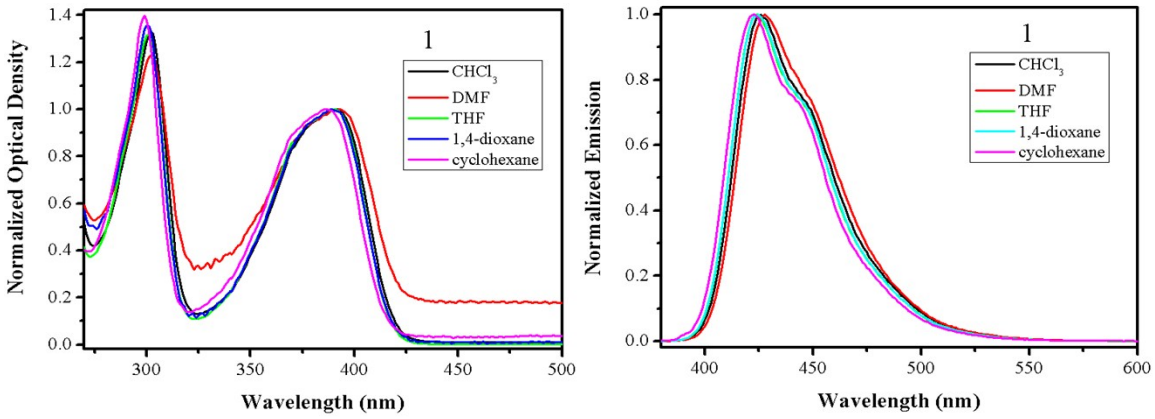


Figure S28. UV-visible absorption (left) and fluorescence (right) spectra of **1** in different solvent environment.

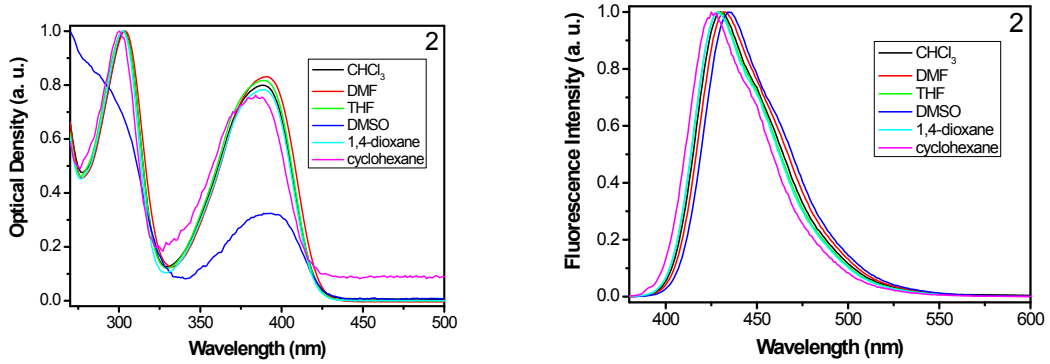


Figure S29. UV-visible absorption (left) and fluorescence (right) spectra of **2** in different solvent environment.

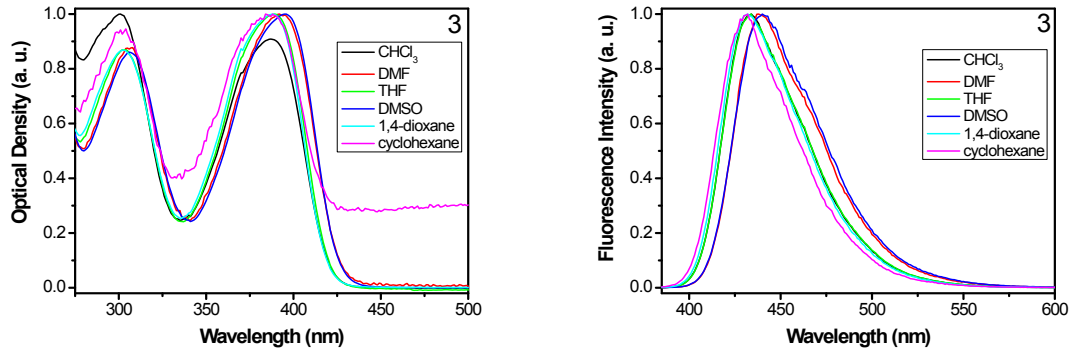


Figure S30. UV-visible absorption (left) and fluorescence (right) spectra of **3** in different solvent environment.

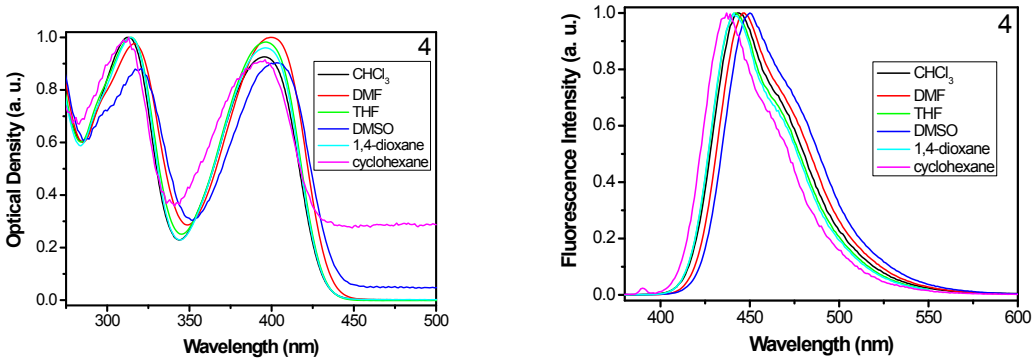


Figure S31. UV-visible absorption (left) and fluorescence (right) spectra of **4** in different solvent environment.

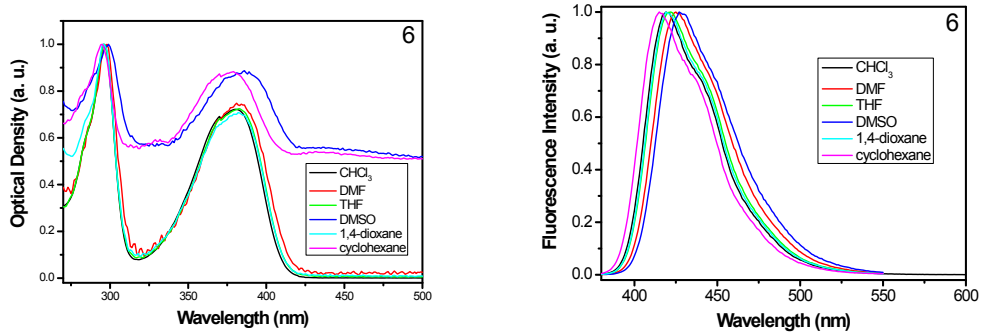


Figure S32. UV-visible absorption (left) and fluorescence (right) spectra of **6** in different solvent environment.

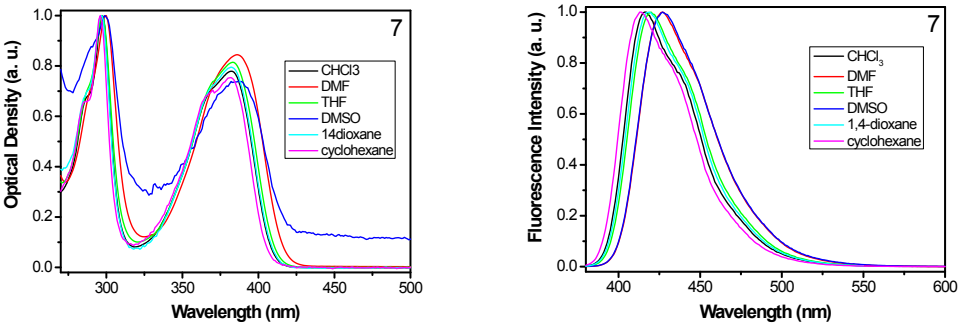


Figure S33. UV-visible absorption (left) and fluorescence (right) spectra of **7** in different solvent environment.

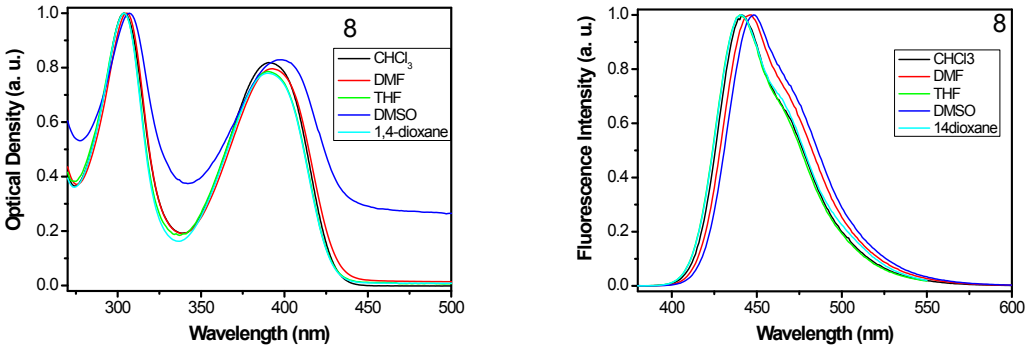


Figure S34. UV-visible absorption (left) and fluorescence (right) spectra of **8** in different solvent environment.

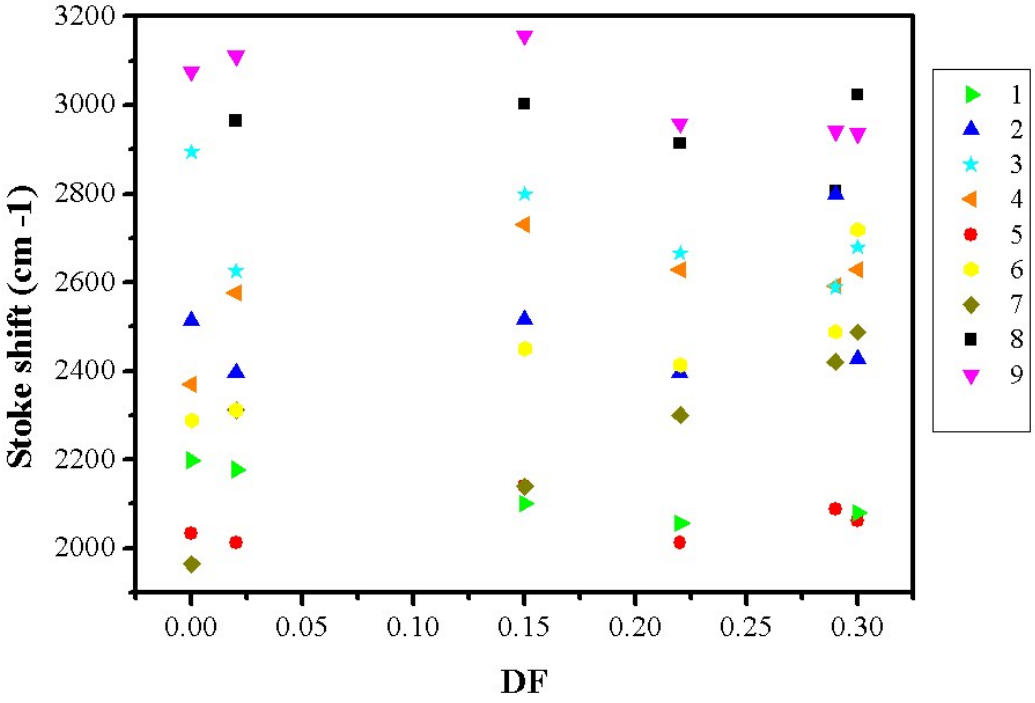


Figure S35. Plot of Stokes shift vs Δf for compounds **1-9**.

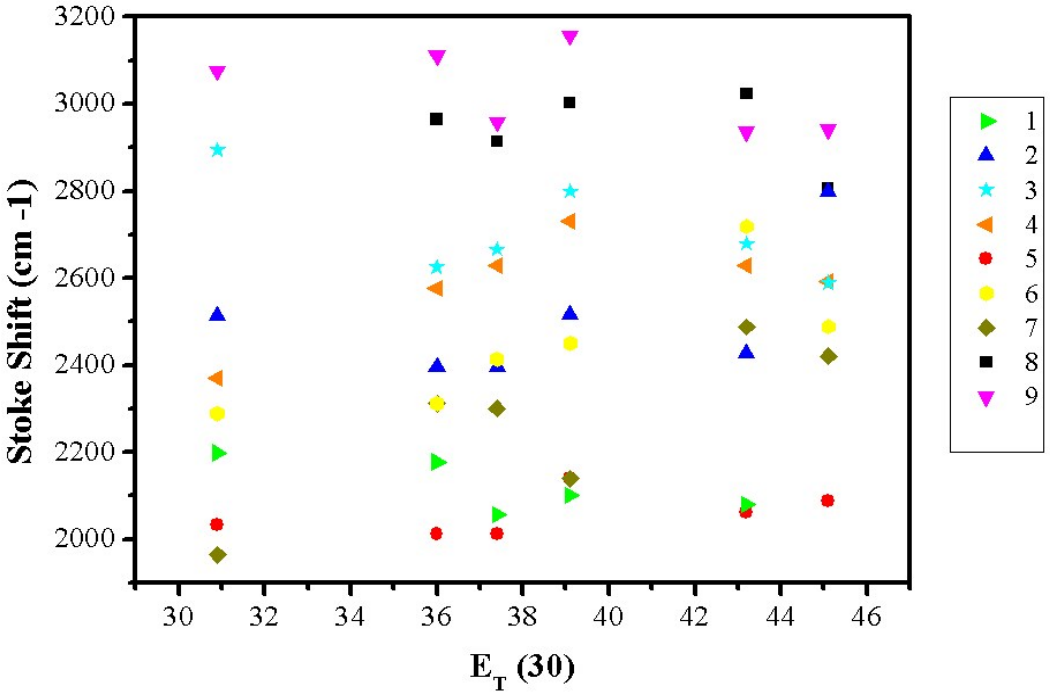


Figure S36. Plot of Stokes shift vs $E_T(30)$ for compounds **1-9**.

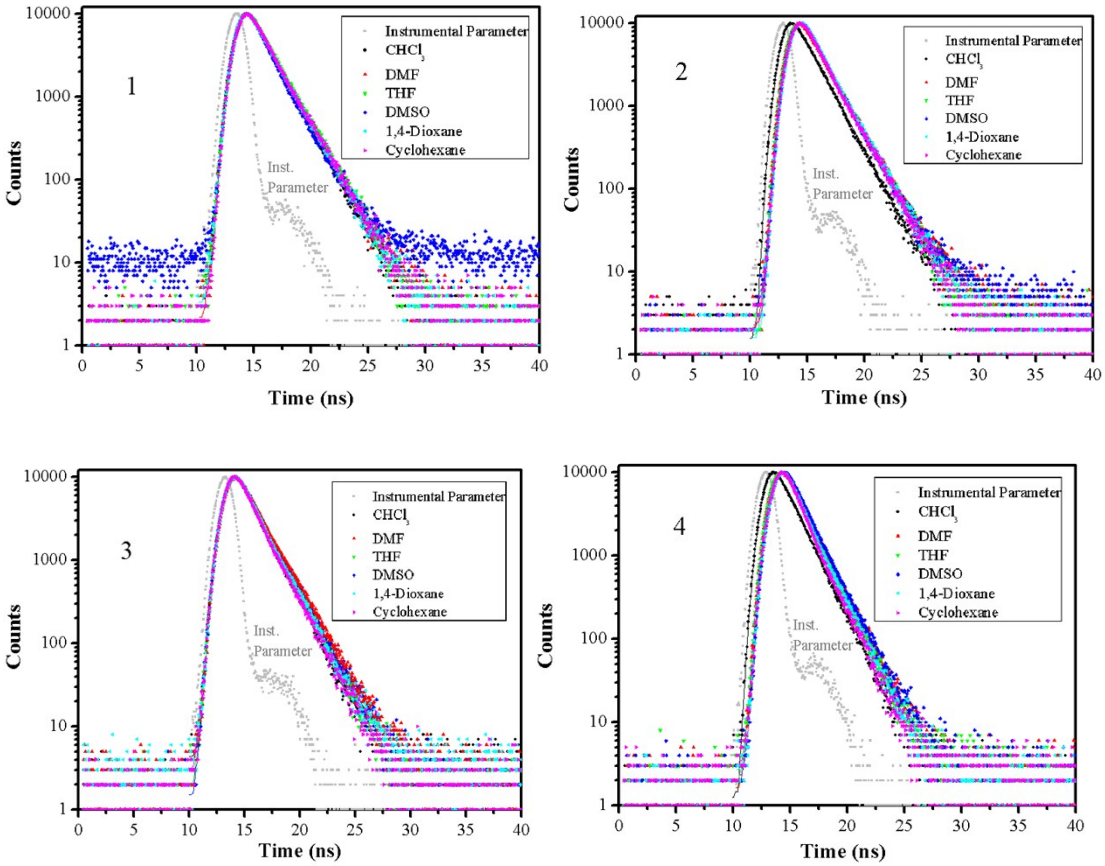


Figure S37. Time-resolved fluorescence decay profile for various compounds **1-4** in different solvents.

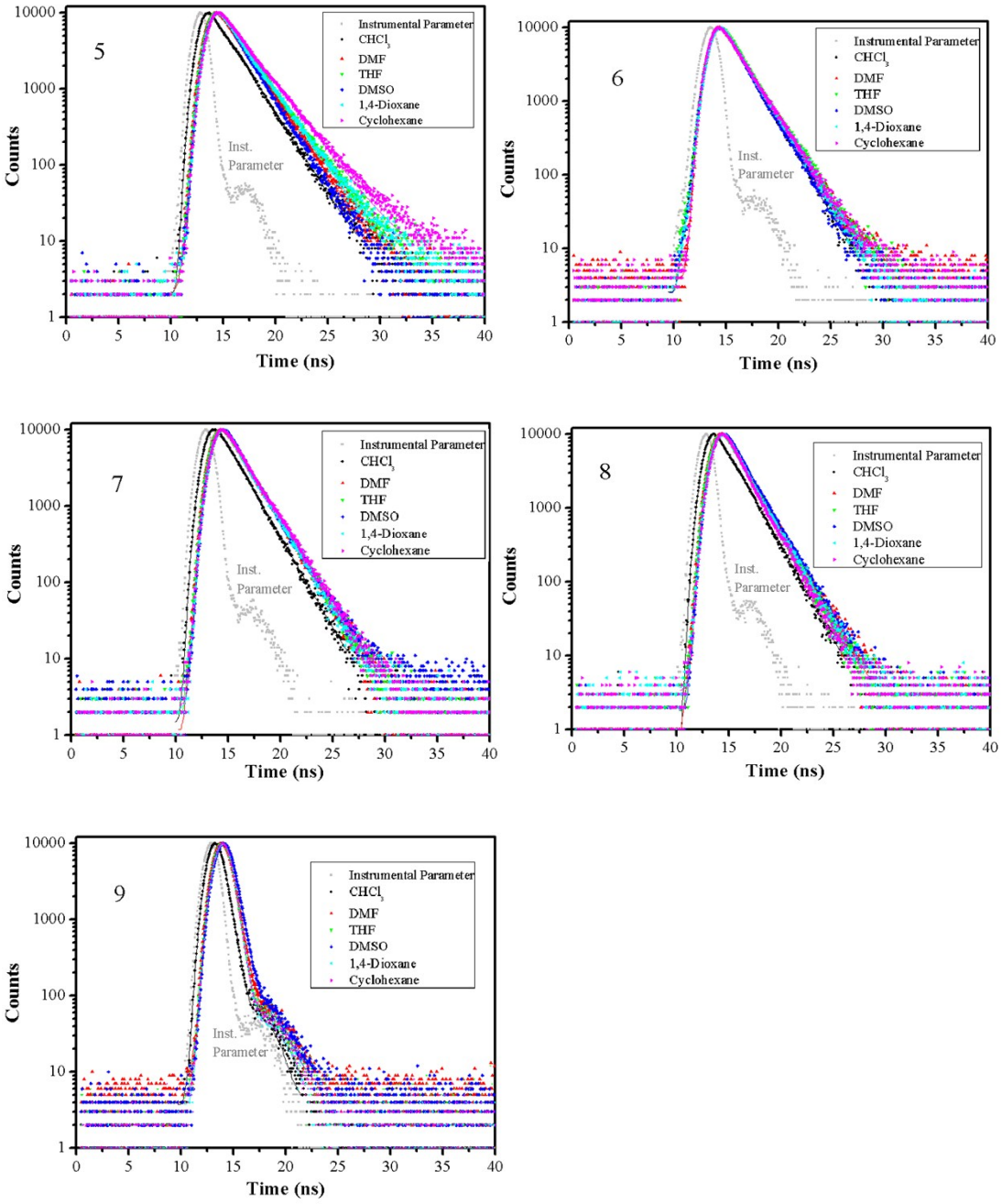


Figure S38. Time-resolved fluorescence decay profile for various compounds **5-9** in different solvents.

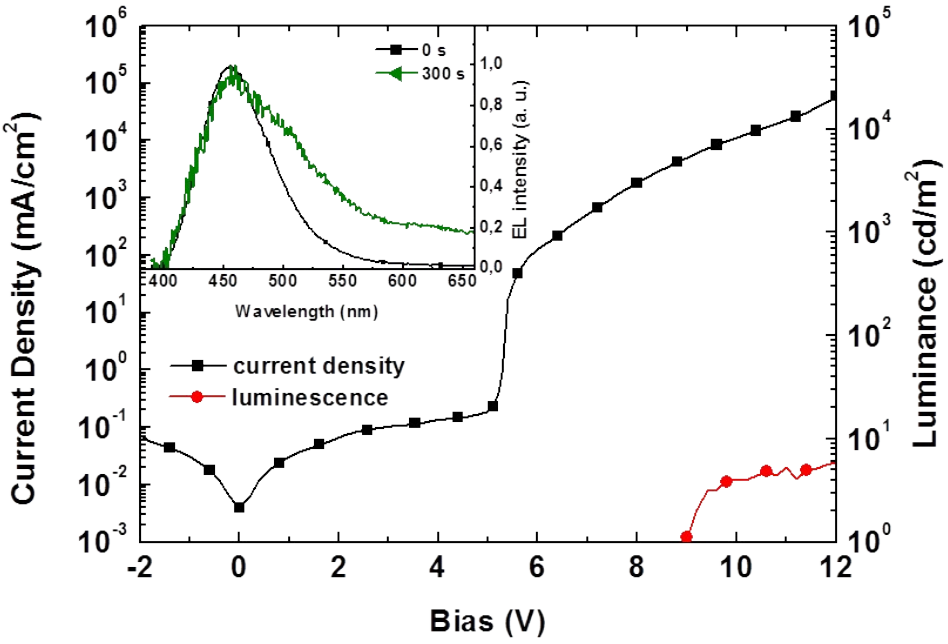


Figure S39. Current density (square) and luminance (circle) as a function of the bias voltage of ITO/PEDOT:PSS/**7**/Ca/Al devices (a) and the time-dependent evolution of the EL emission profile over the course of 5 min of continuous operation of **7** at an applied current density of $3x10^4$ mA cm^{-2} respectively.

Table S1. Absorption, emission maxima and stokes shifts of **1-9** in chloroform.

Compound	Solvent	λ_{max}^{em} (in nm)	λ_{max}^{abs} (in nm)	$\Delta\lambda$ (in cm^{-1})
1	Chloroform	426	391	2101
2	Chloroform	430	388	2517
3	Chloroform	434	387	2798
4	Chloroform	444	396	2730
5	Chloroform	416	382	2140
6	Chloroform	419	380	2449
7	Chloroform	416	382	2140
8	Chloroform	443	391	3002
9	Chloroform	467	407	3157

Table S2. Absorption, emission maxima and stokes shifts of **1-9** in 1,4-dioxane.

Compound	Solvent	λ_{max}^{em} (in nm)	λ_{max}^{abs} (in nm)	$\Delta\lambda$ (in cm^{-1})
1	1,4-dioxane	425	389	2178
2	1,4-dioxane	429	389	2397
3	1,4-dioxane	432	388	2625
4	1,4-dioxane	441	396	2577
5	1,4-dioxane	415	383	2013
6	1,4-dioxane	419	382	2312
7	1,4-dioxane	419	382	2312
8	1,4-dioxane	441	390	2965
9	1,4-dioxane	466	407	3111

Table S3. Absorption, emission maxima and stokes shifts of **1-9** in THF.

Compound	Solvent	λ_{max}^{em} (in nm)	λ_{max}^{abs} (in nm)	$\Delta\lambda$ (in cm^{-1})
1	THF	424	390	2056
2	THF	429	389	2397
3	THF	434	389	2665
4	THF	442	396	2628
5	THF	415	383	2013
6	THF	422	383	2413
7	THF	420	383	2300
8	THF	440	390	2914
9	THF	464	408	2958

Table S4. Absorption, emission maxima and stokes shifts of **1-9** in DMF.

Compound	Solvent	λ_{max}^{em} (in nm)	λ_{max}^{abs} (in nm)	$\Delta\lambda$ (in cm^{-1})
1	DMF	428	393	2081
2	DMF	432	391	2427
3	DMF	438	392	2679
4	DMF	447	400	2629
5	DMF	417	384	2061
6	DMF	425	381	2717
7	DMF	427	386	2488
8	DMF	446	393	3024
9	DMF	470	413	2936

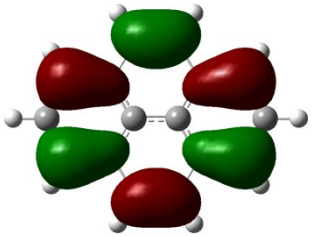
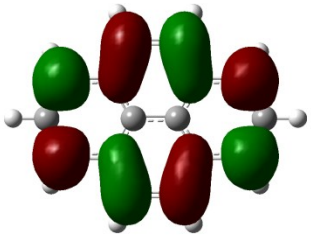
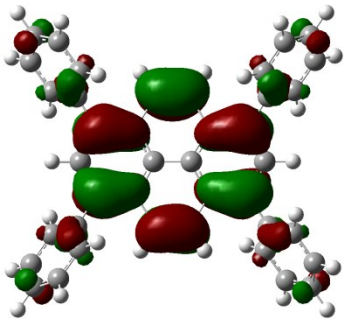
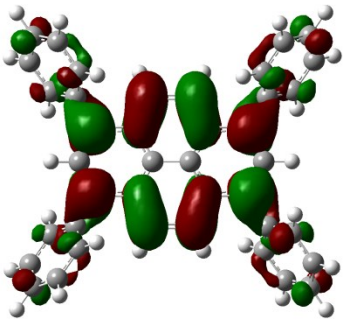
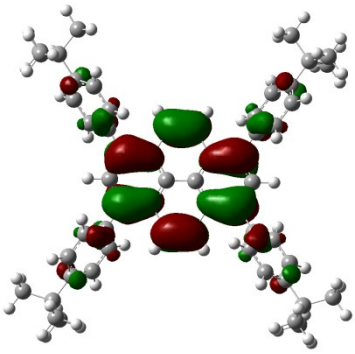
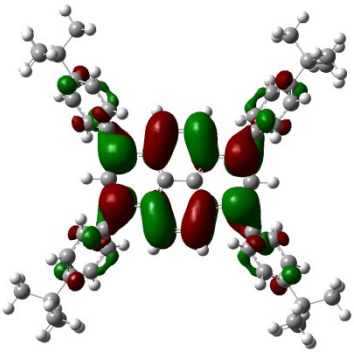
Table S5. Absorption, emission maxima and stokes shift of **1-9** in cyclohexane.

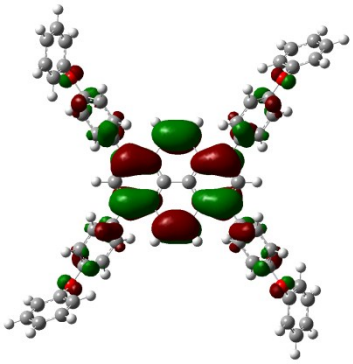
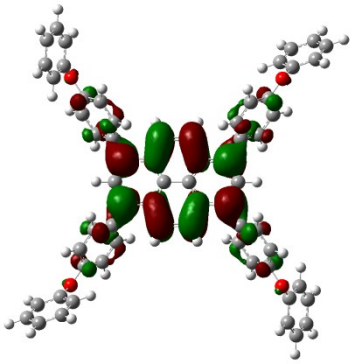
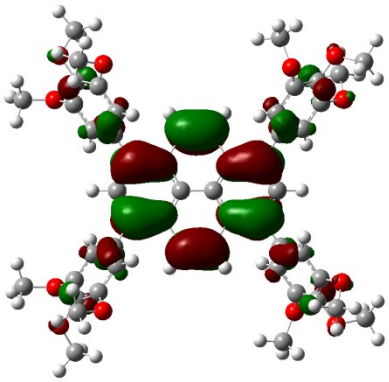
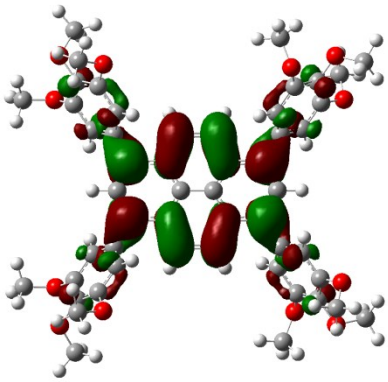
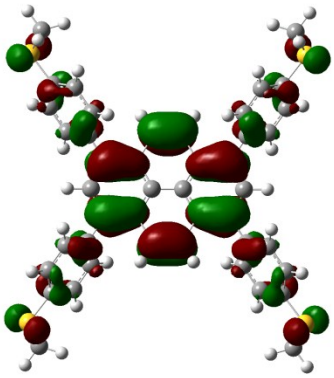
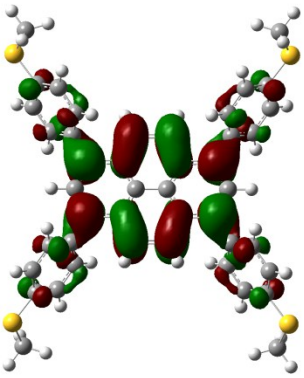
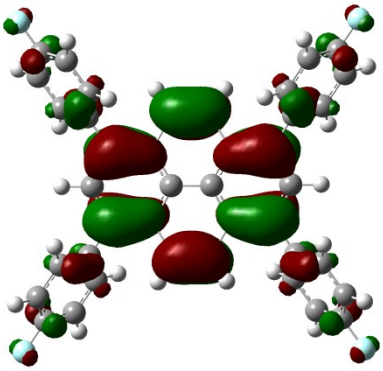
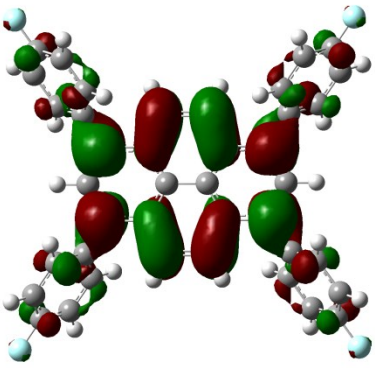
Compound	Solvent	λ_{max}^{em} (in nm)	λ_{max}^{abs} (in nm)	$\Delta\lambda$ (in cm^{-1})
1	cyclohexane	423	387	2199
2	cyclohexane	425	384	2512
3	cyclohexane	432	384	2894
4	cyclohexane	437	396	2369
5	cyclohexane	413	381	2034
6	cyclohexane	415	379	2289
7	cyclohexane	413	382	1965
8	cyclohexane	NON SOLUBLE		
9	cyclohexane	460	403	3075
TPP	cyclohexane	n.d.	n.d.	3220
Pyrene	cyclohexane	n.d.	n.d.	3360

Table S6. Absorption, emission maxima and stokes shift of **1-9** in DMSO.

Compound	Solvent	λ_{max}^{em} (in nm)	λ_{max}^{abs} (in nm)	$\Delta\lambda$ (in cm^{-1})
1	DMSO	NON SOLUBLE		
2	DMSO	434	387	2798
3	DMSO	440	395	2589
4	DMSO	450	403	2592
5	DMSO	421	387	2087
6	DMSO	427	386	2488
7	DMSO	427	387	2421
8	DMSO	448	398	2804
9	DMSO	474	416	2941

Table S7. Frontier molecular orbitals depiction involved in the $S_0 \rightarrow S_1$ ($S_0 \rightarrow S_2$ for the case of pyrene) vertical transitions of pyrene, TPP, and **1** – **9** as calculated at the ωB97/6-31G(d,p) level of theory.

	HOMO	**LUMO**
Pyrene		
TPP		
1		

2		
3		
4		
5		

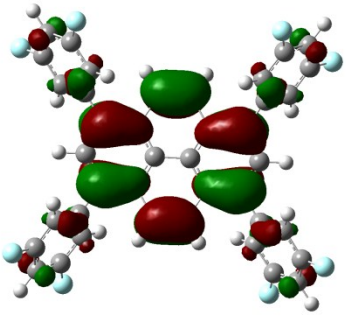
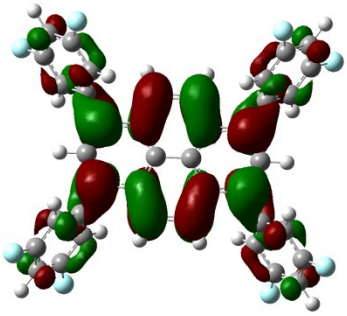
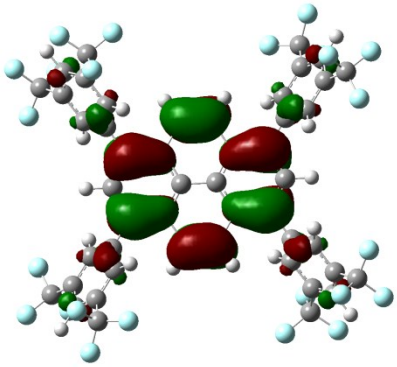
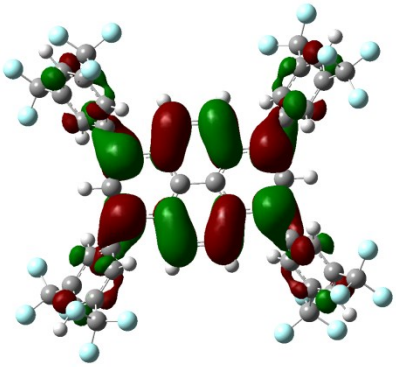
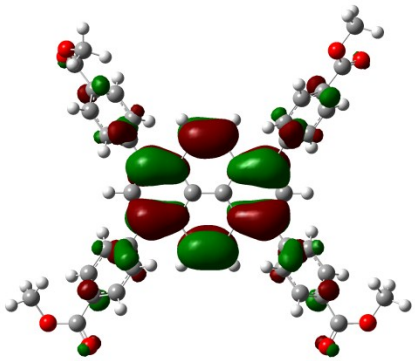
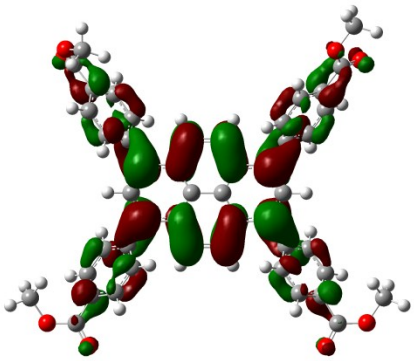
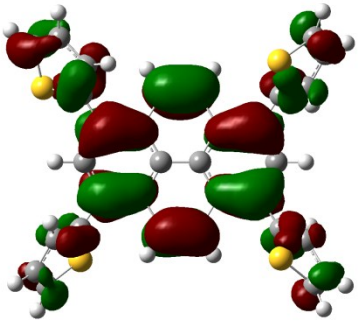
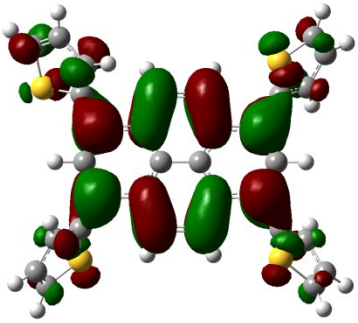
6		
7		
8		
9		

Table S8. Melting points (T_m) and decomposition temperature (T_d, at 5% decomposition) for pyrene, TPP, and **1** – **9**.

Compound	Substituent	T_m (°C) +/- 0.5	T_d (°C)
Pyrene	--	150.4 (Lit[1] 151)	211.3
TPP (1,3,6,8-tetraphenylpyrene)	-H	299.4	372.0
1	*tert*-butyl	>410.0	439.1
2	$-OC_6H_5$	276.1	503.6
3	$-OCH_3$ (x 3)	325.0	408.7
4	$-SCH_3$	318.5	392.4
5	-F	309.0	381.8
6	-F (x 2)	> T_d	368.2
7	$-CF_3$ (x 2)	314.7	318.4
8	$-CO_2CH_3$	345.8	410.0
9	thienyl	306.4 (Lit[2] 308)	400.1

1. J. Yoon, A. J. Lesser and T. J. McCarthy, *PMSE Prepr.*, 2007, **97**, 742.
2. H. Zhang, Y. Wang, K. Shao, Y. Liu, S. Chen, W. Qiu, X. Sun, T. Qi, Y. Ma, G. Yu, Z. Su and D. Zhu, Chem. Commun. 2006, 755-757.