Fine-Tuning the Electronic Properties of Azo Chromophore-Incorporated Perylene Bisimide Dyads

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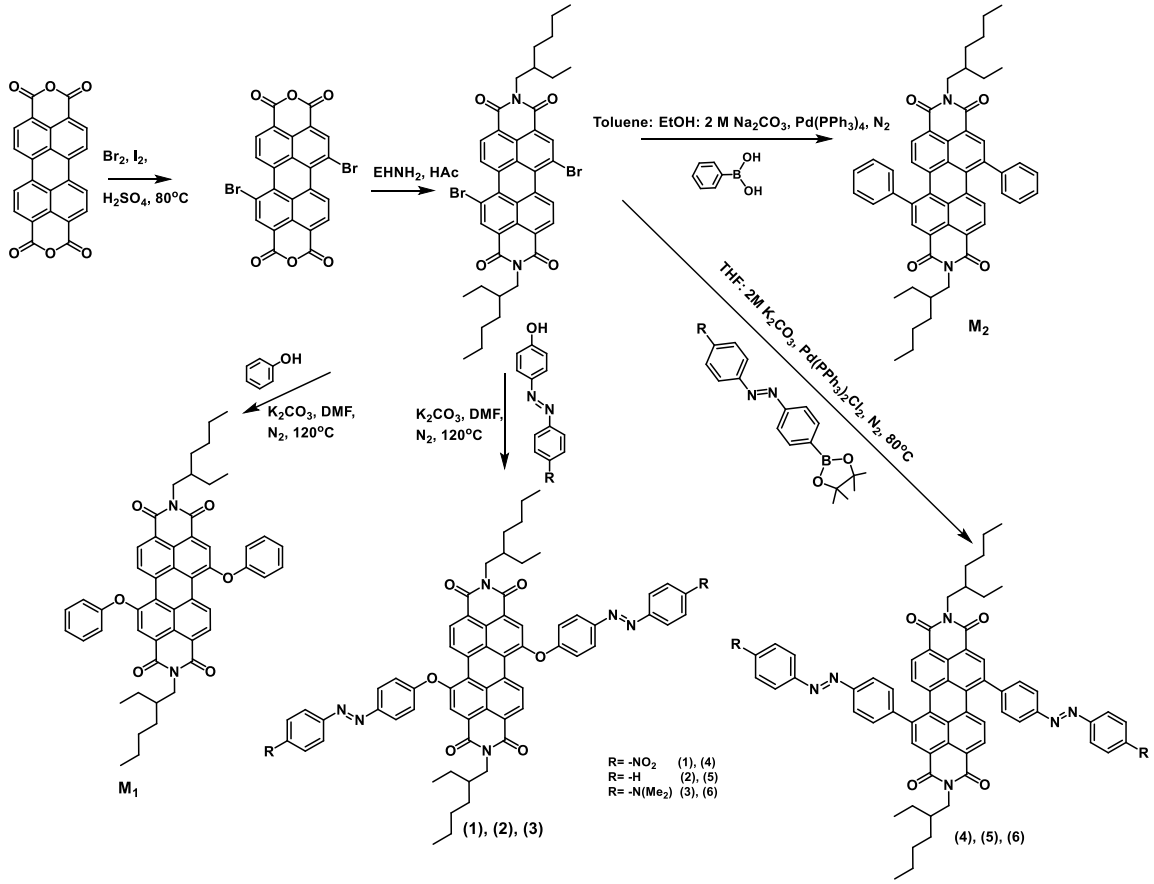
Supporting Information

Contents

Scheme S 1. Detailed synthetic pathway to azobenzene incorporated and model PBIs.



1. Detailed Characterization of Synthesized Compounds

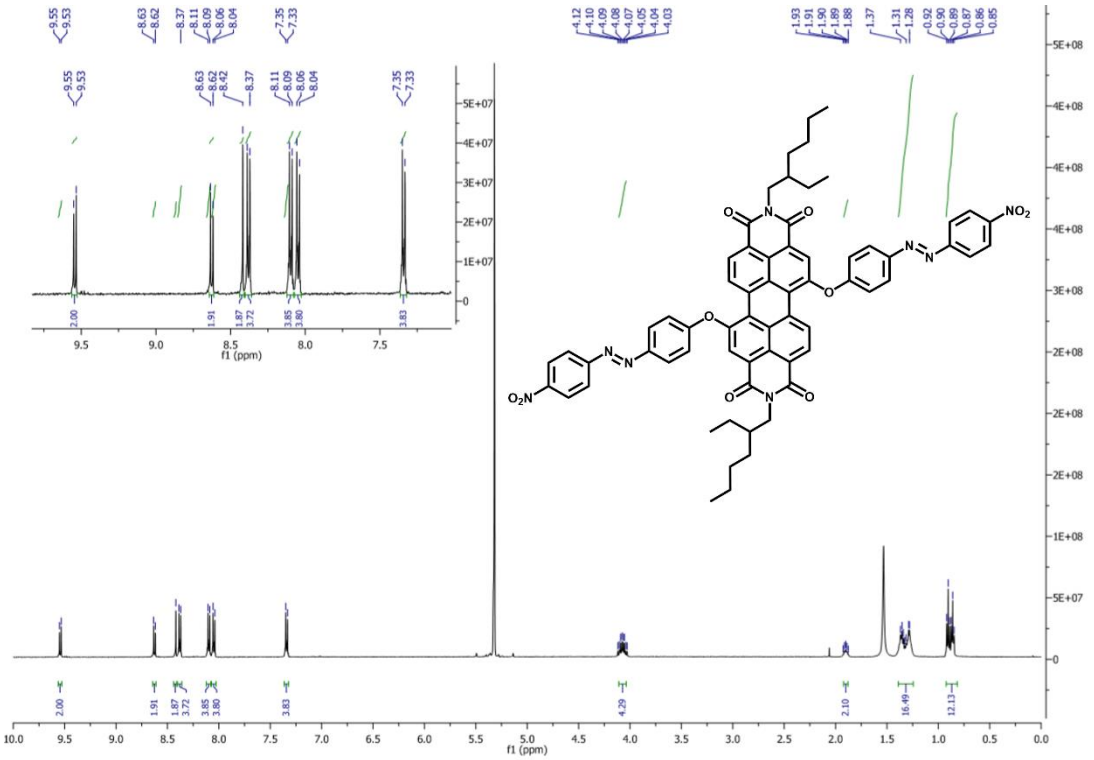


Figure S 1. ^{1}H NMR (500 MHz) spectra of **(1)** in CD_2Cl_2.

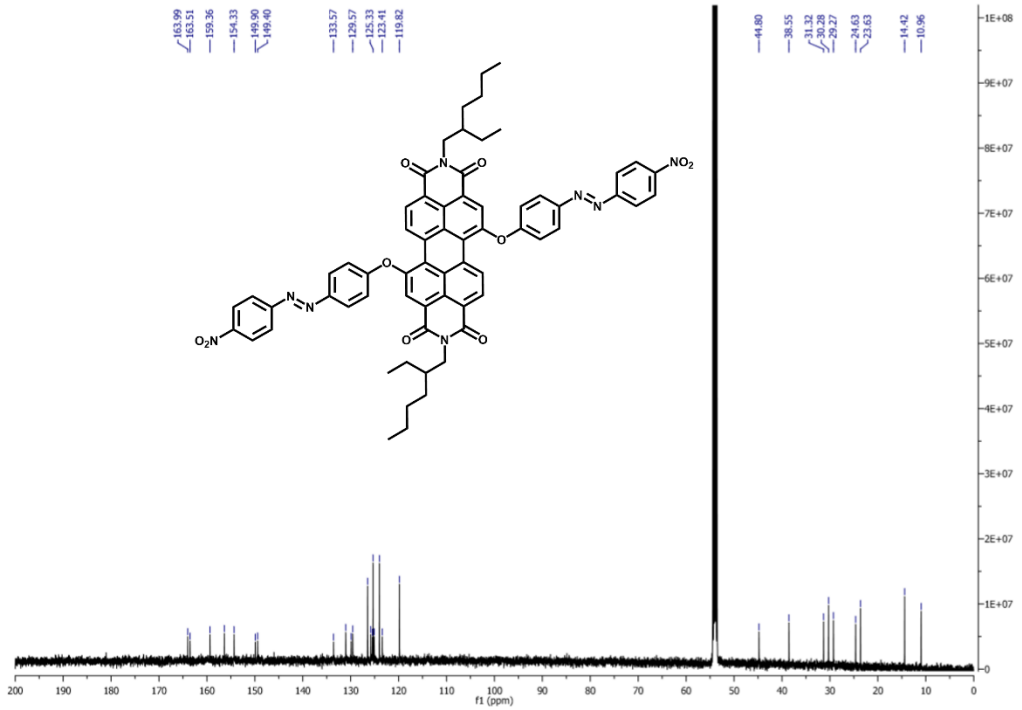


Figure S 2. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectra of **(1)** in CD_2Cl_2.

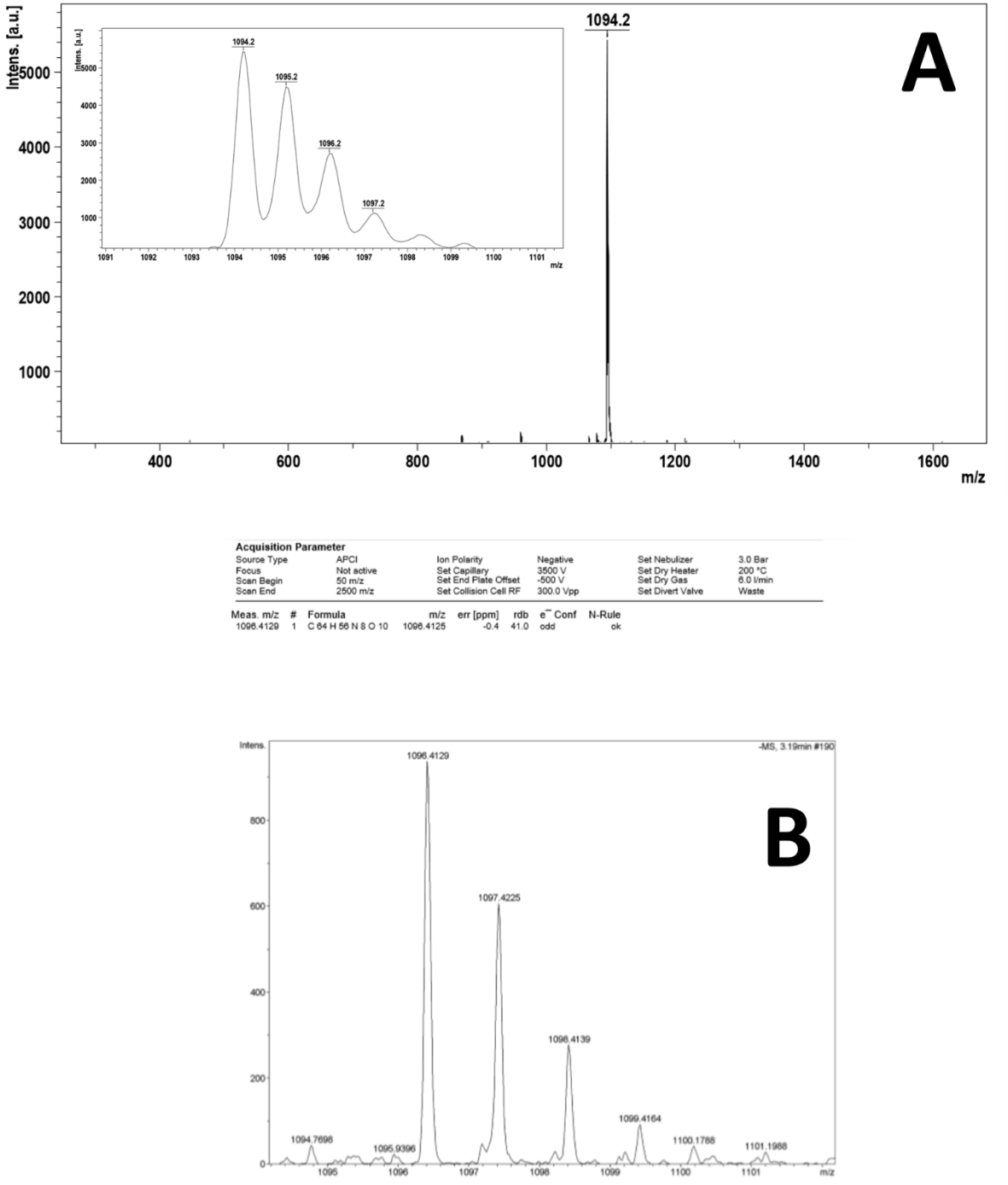


Figure S 3. MS analysis of **(1)**: MALDI-TOF spectra (A) and HRMS (APCI-TOF) spectra (B) in negative ion polarity.

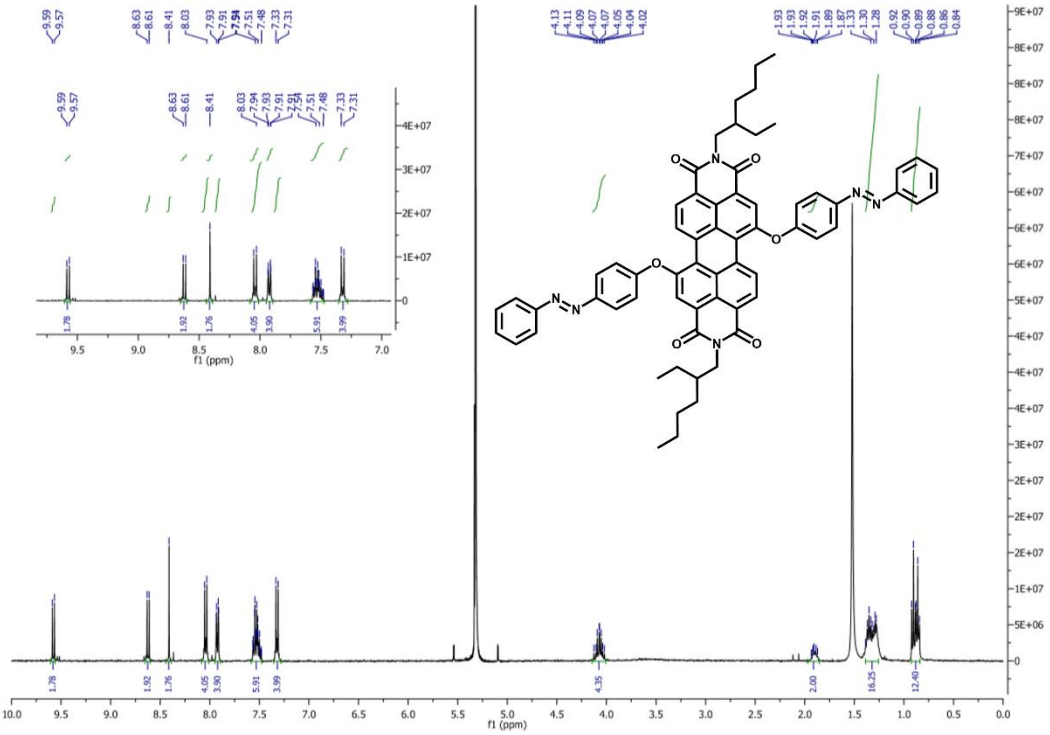


Figure S 4. ^{1}H NMR (400 MHz) spectra of **(2)** in CD_2Cl_2.

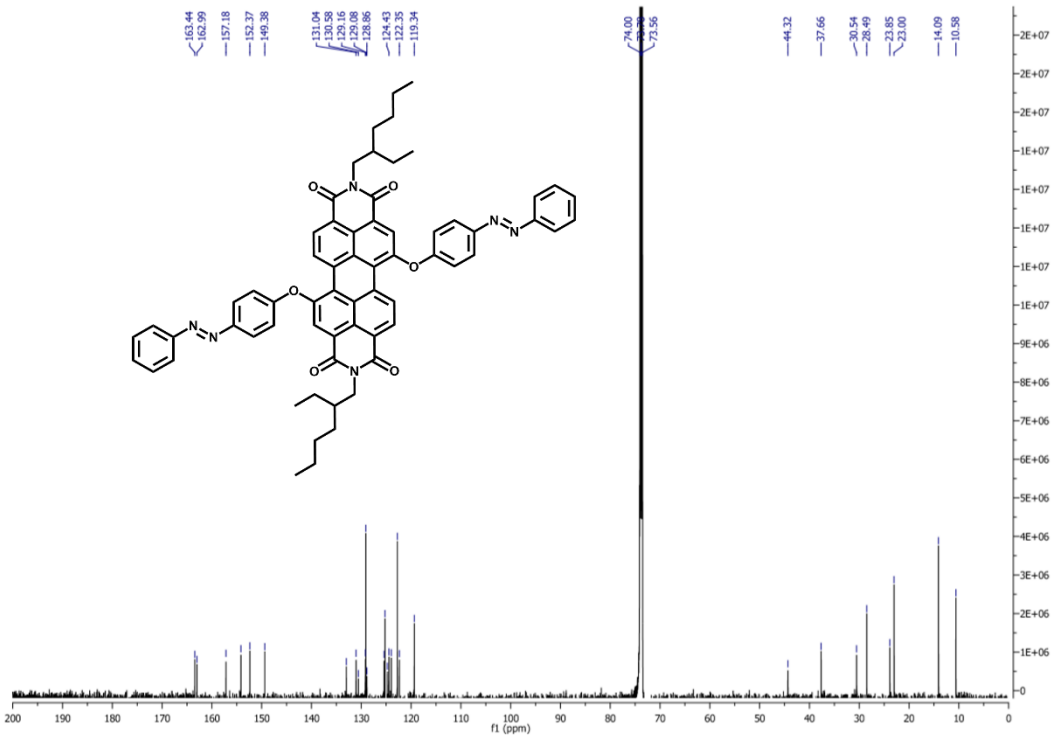
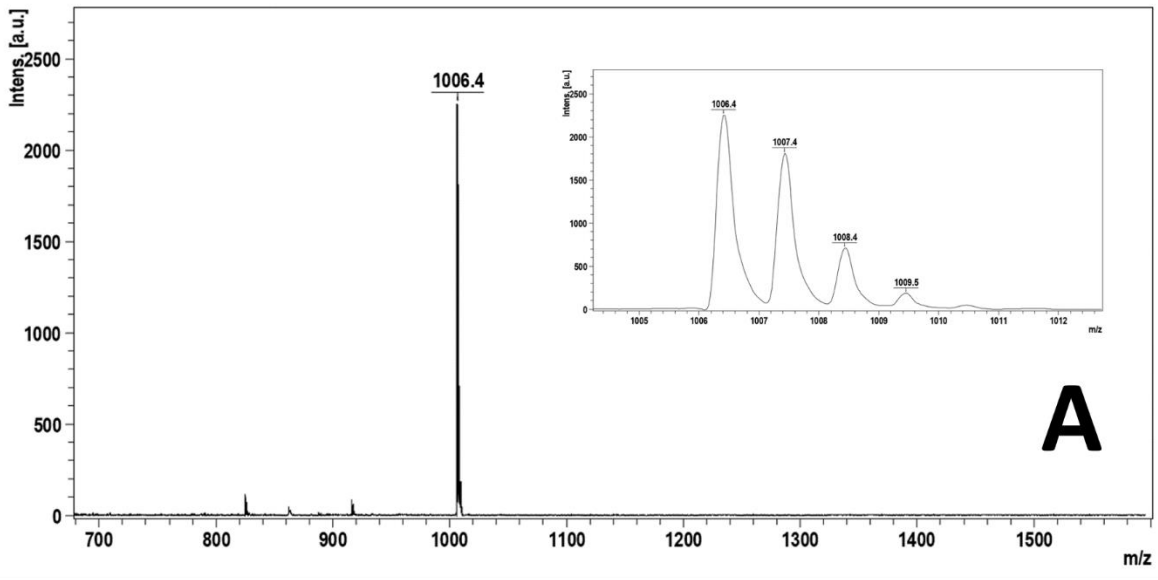


Figure S 5. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectra of **(2)** in 1,1,2,2-tetrachloroethane-d_2.



Acquisition Parameter

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Scan End	2500 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
1006.4430	1	C 64 H 58 N 6 O 6	1006.4423	-0.6	39.0	odd	ok

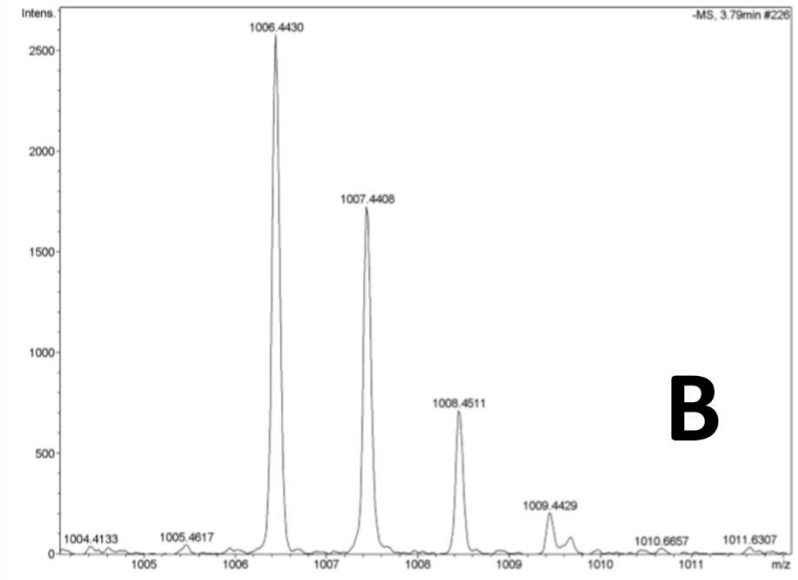


Figure S 6. MS analysis of **(2)**: MALDI-TOF spectra (A) and HRMS (APCI-TOF) spectra (B) in negative ion polarity.

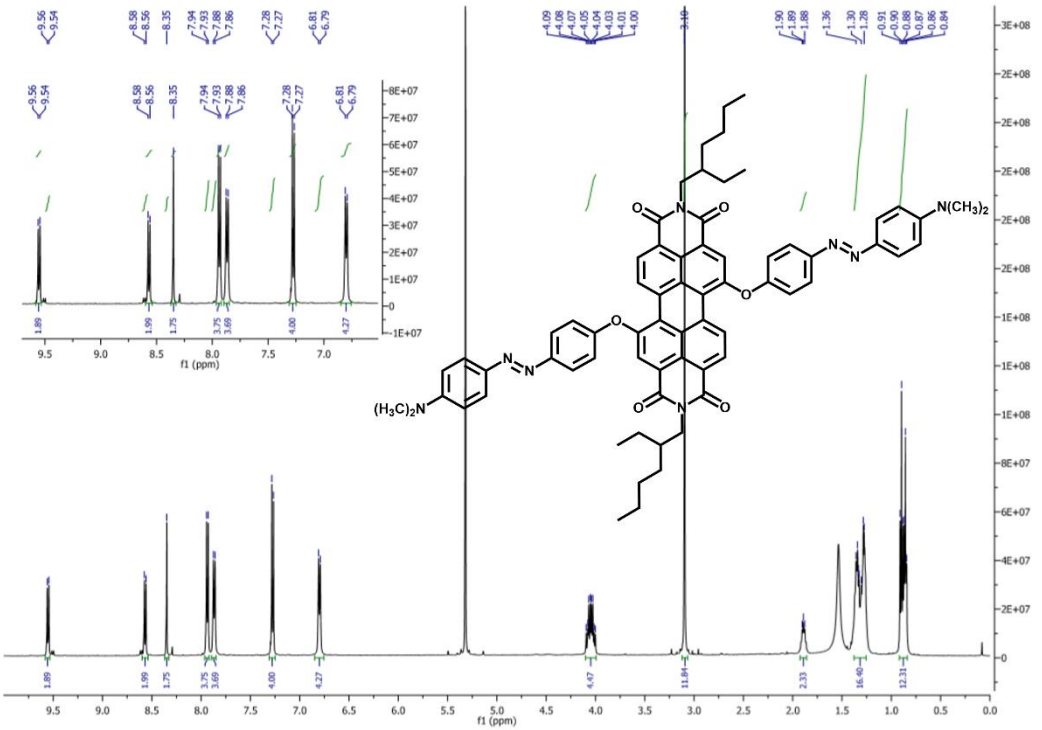


Figure S 7. ^{1}H NMR (500 MHz) spectra of **(3)** in CD_2Cl_2.

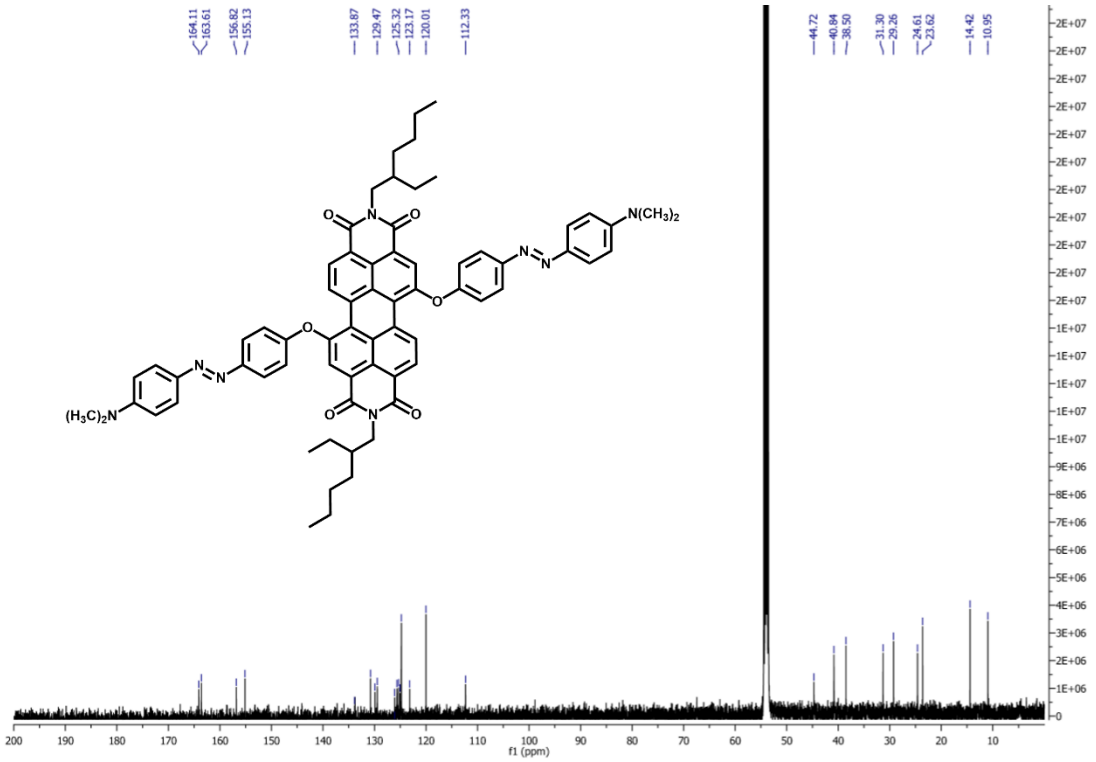
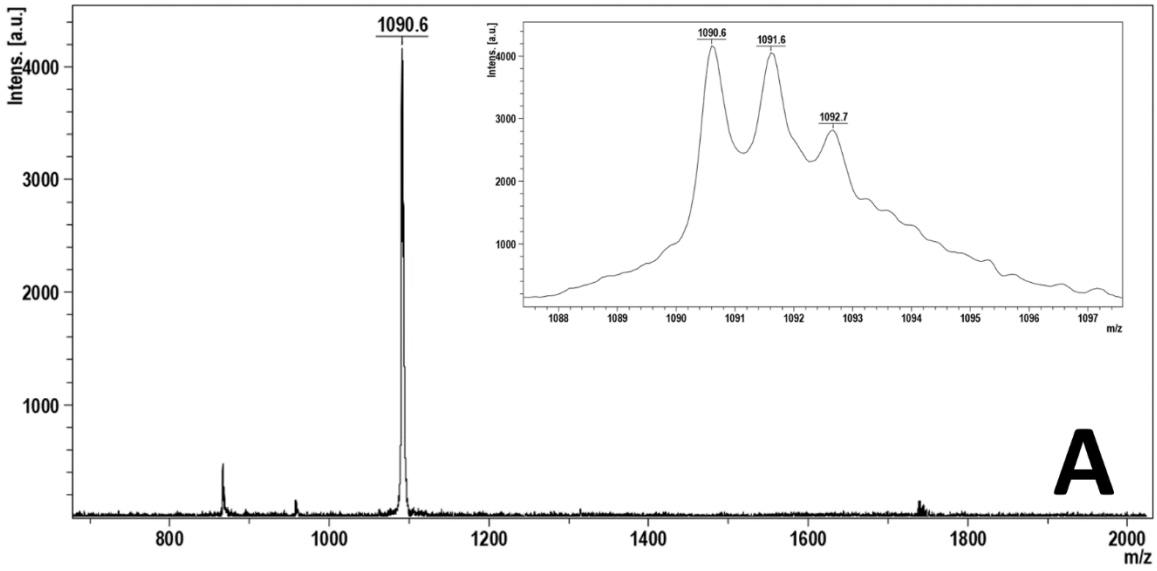


Figure S 8. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectra of **(3)** in CD_2Cl_2.



Acquisition Parameter					
Source Type	APCI	Ion Polarity	Negative	Set Nebulizer	3.0 Bar
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Scan End	2500 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e¯ Conf	N-Rule
1127.4957	1	C 68 H 68 Cl N 8 O 6	1127.4956	-0.1	38.5	even	ok

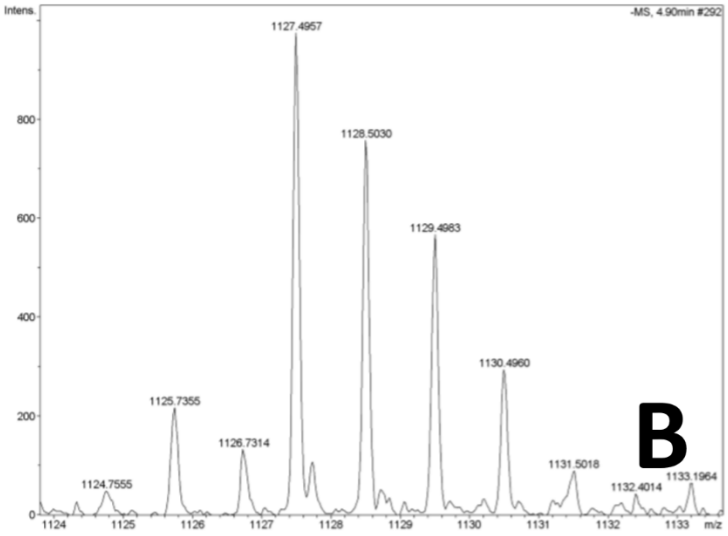


Figure S 9. MS analysis of **(3)**: MALDI-TOF spectra (A) and HRMS (APCI-TOF) spectra (B) in negative ion polarity.

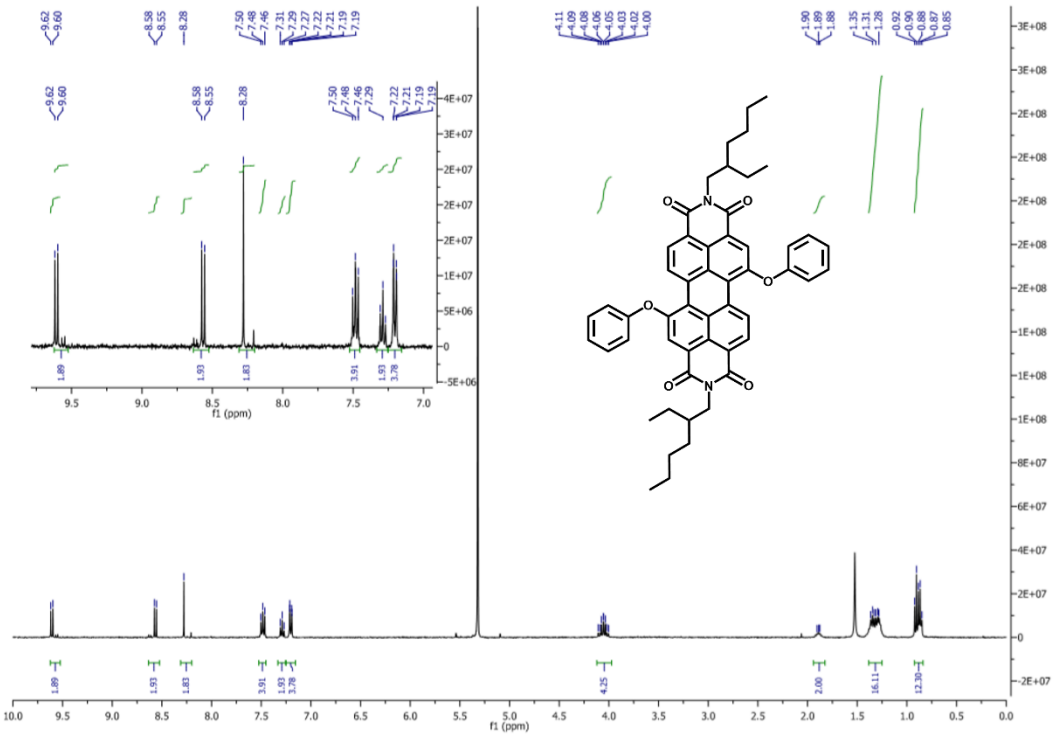


Figure S 10. ^{1}H NMR (400 MHz) spectra of **M₁** in CD_2Cl_2.

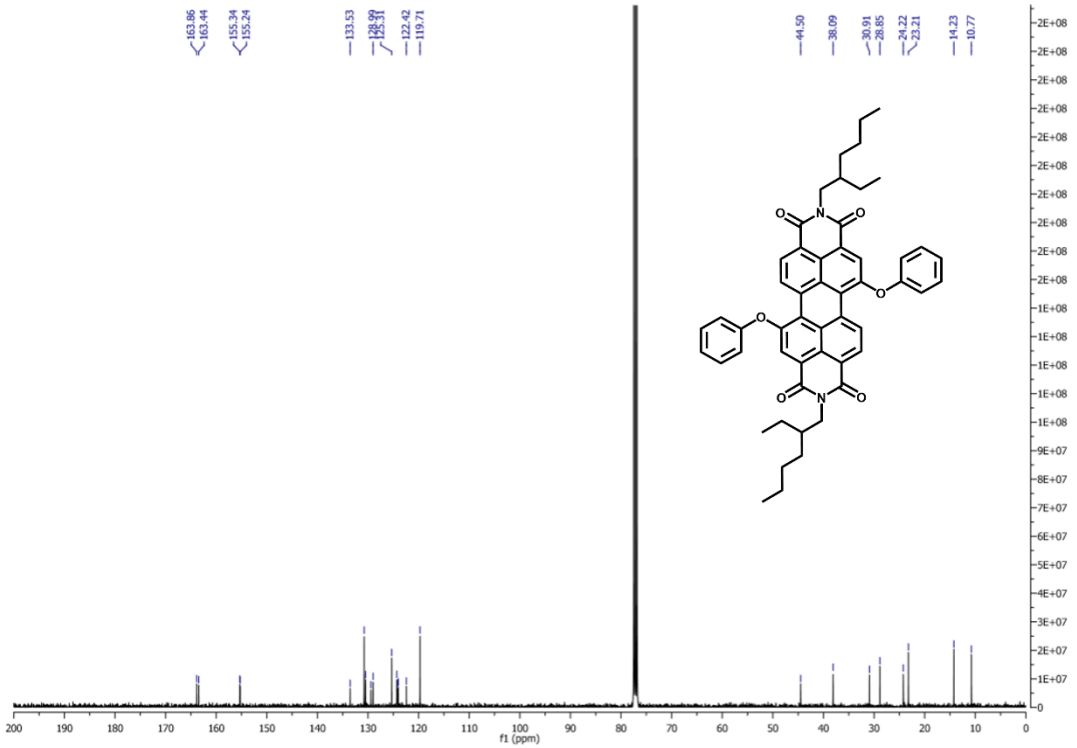
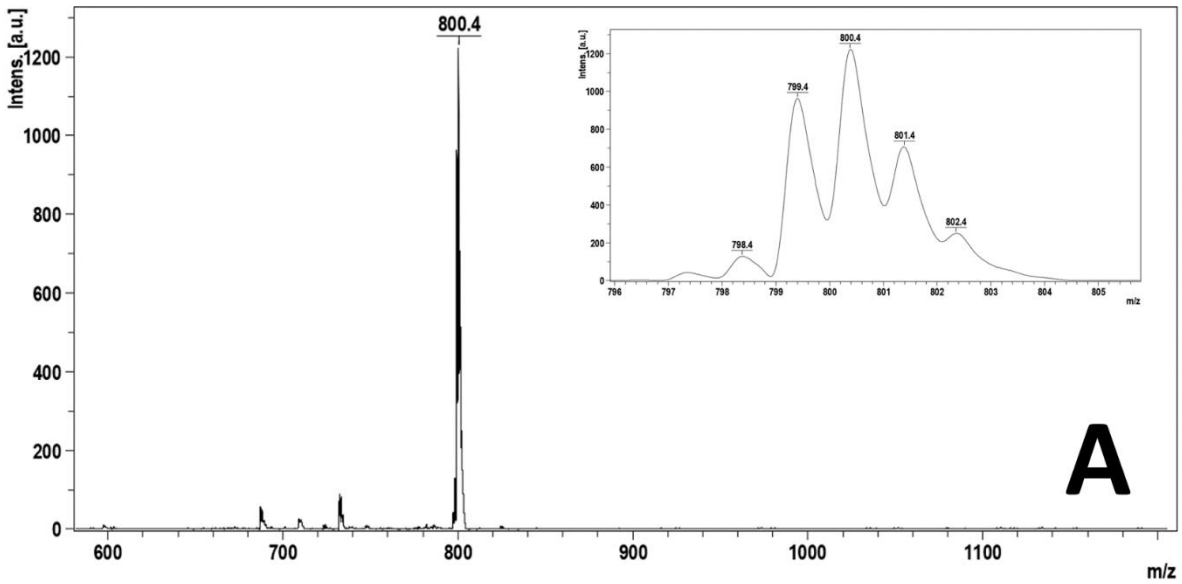


Figure S 11. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectra of **M₁** in CD_2Cl_2.



Acquisition Parameter

Source Type	APCI	Ion Polarity	Negative	Set Nebulizer	3.0 Bar
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Scan End	2500 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
798.3679	1	C 52 H 50 N 2 O 6	100.00	798.3674	-0.5	-0.6	9.8	29.0	odd	ok

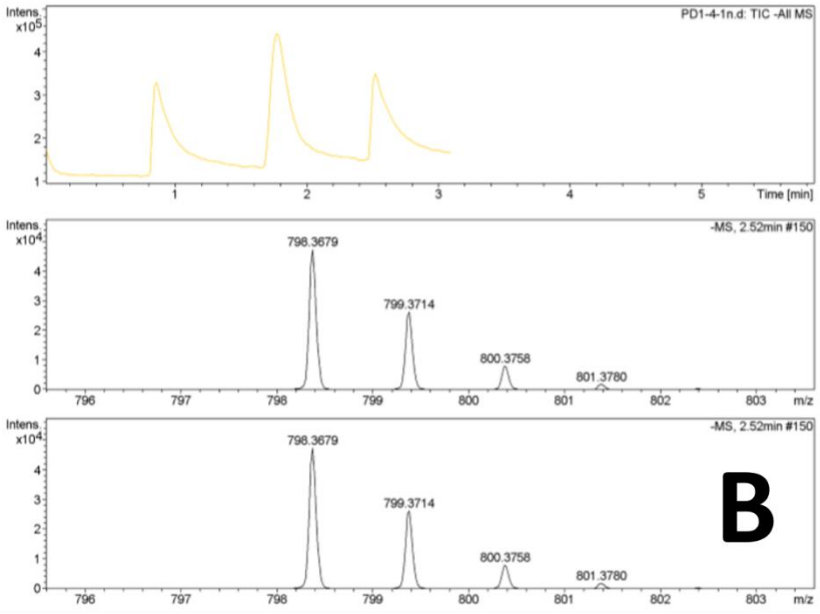


Figure S 12. MS analysis of **M$_1$**: MALDI-TOF spectra in positive ion polarity (A) and HRMS (APCI-TOF) spectra (B) in negative ion polarity.

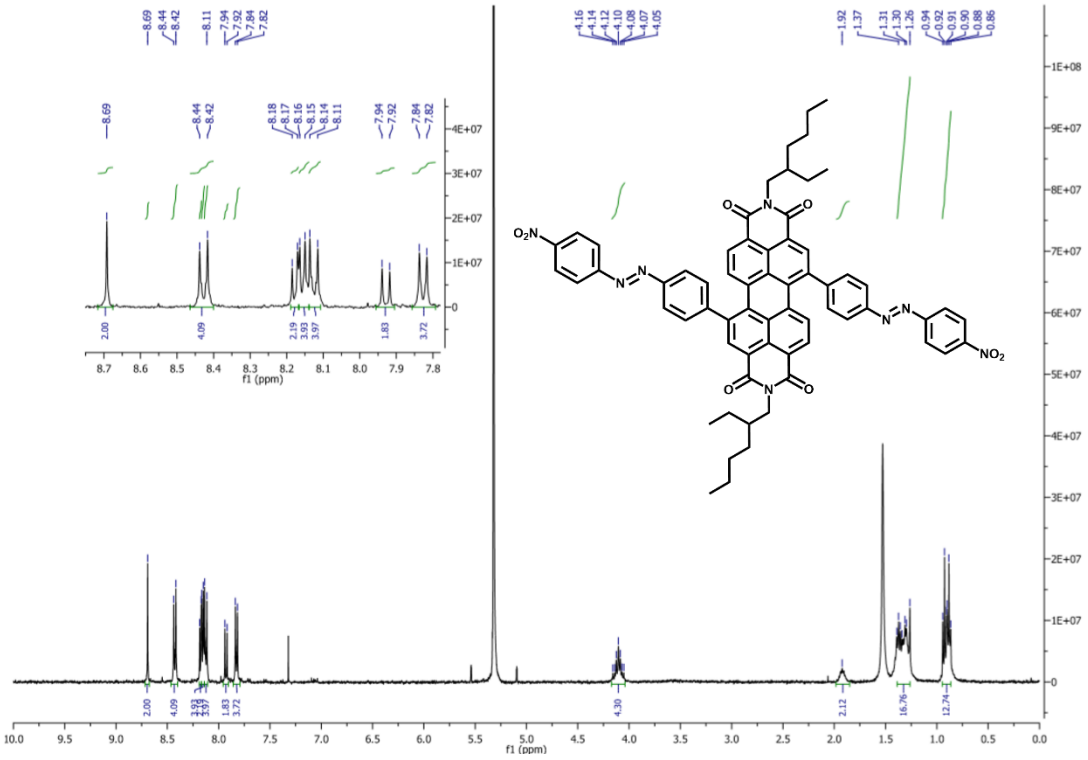


Figure S 13. ^{1}H NMR (400 MHz) spectra of **(4)** in CD_2Cl_2.

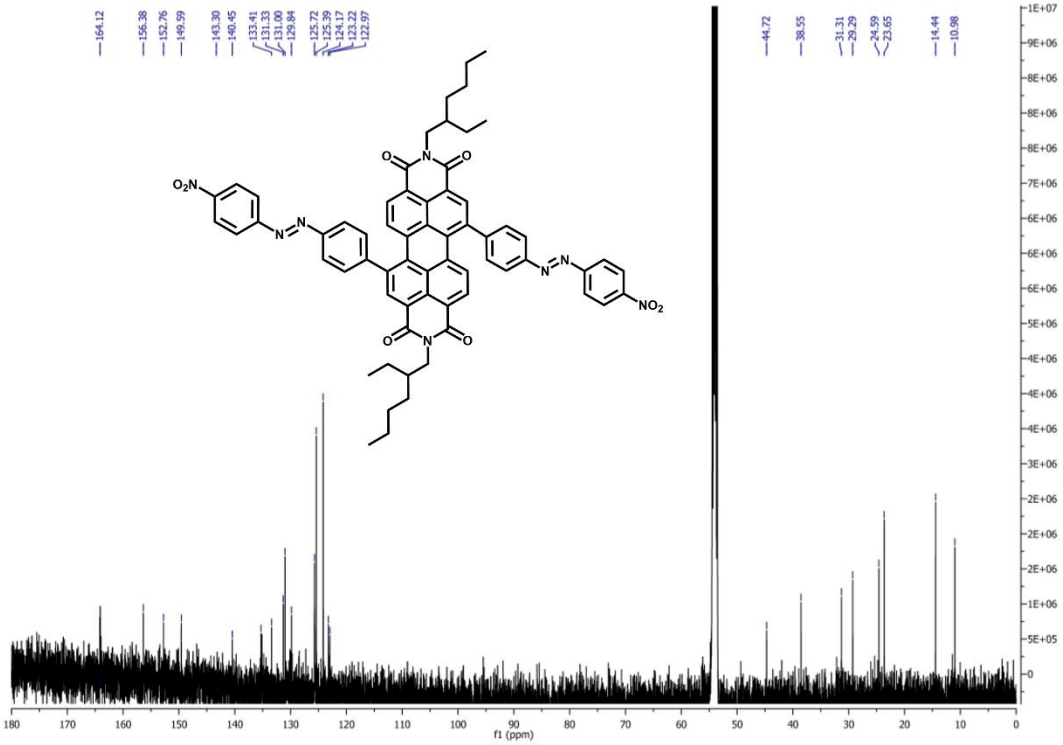
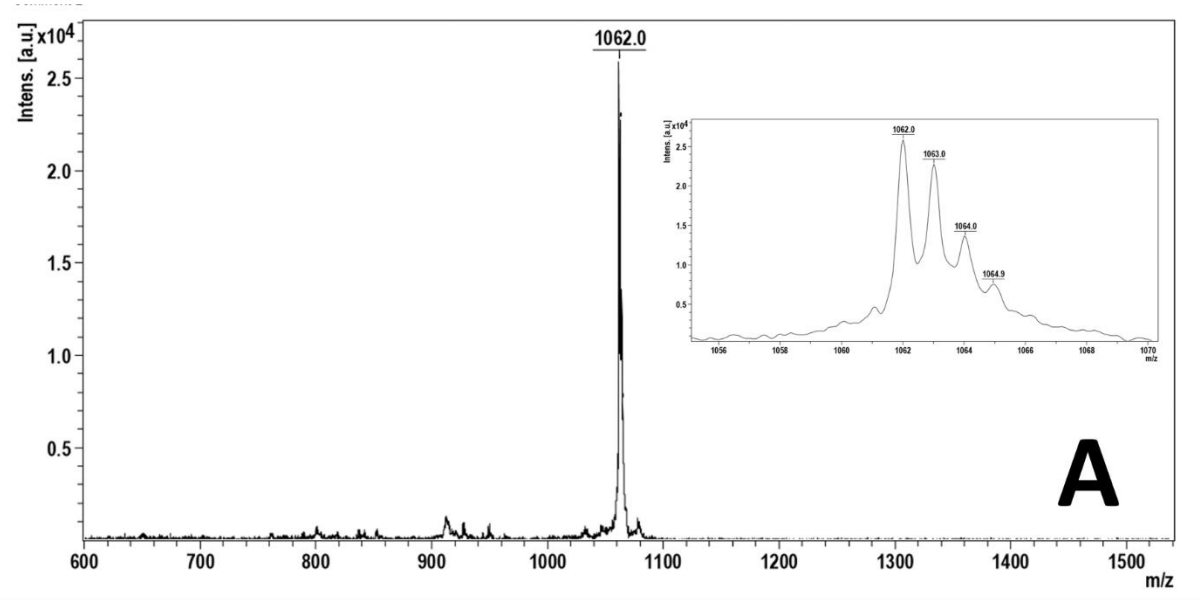


Figure S 14. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectra of **(4)** in CD_2Cl_2.



Acquisition Parameter

Source Type	APCI	Ion Polarity	Negative	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	3500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	8.0 l/min
Scan End	2500 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
1099.3921	1	C 64 H 56 Cl N 8 O 8	1099.3915	-0.5	40.5	even	ok

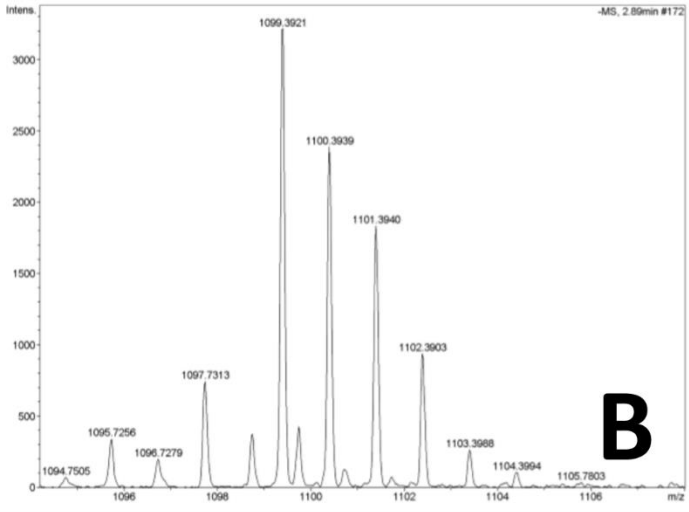


Figure S 15. MS analysis of **(4)**: MALDI-TOF spectra (A) and HRMS (APCI-TOF) spectra (B) in negative ion polarity.

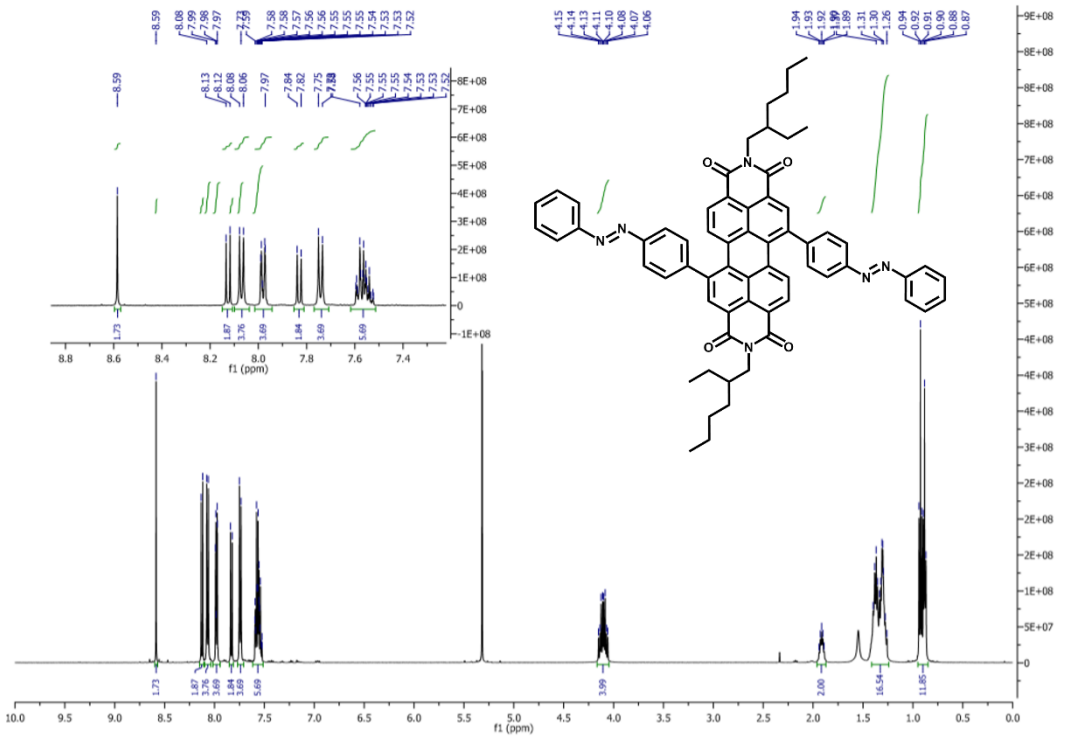


Figure S 16. ^{1}H NMR (500 MHz) spectra of **(5)** in CD_2Cl_2.

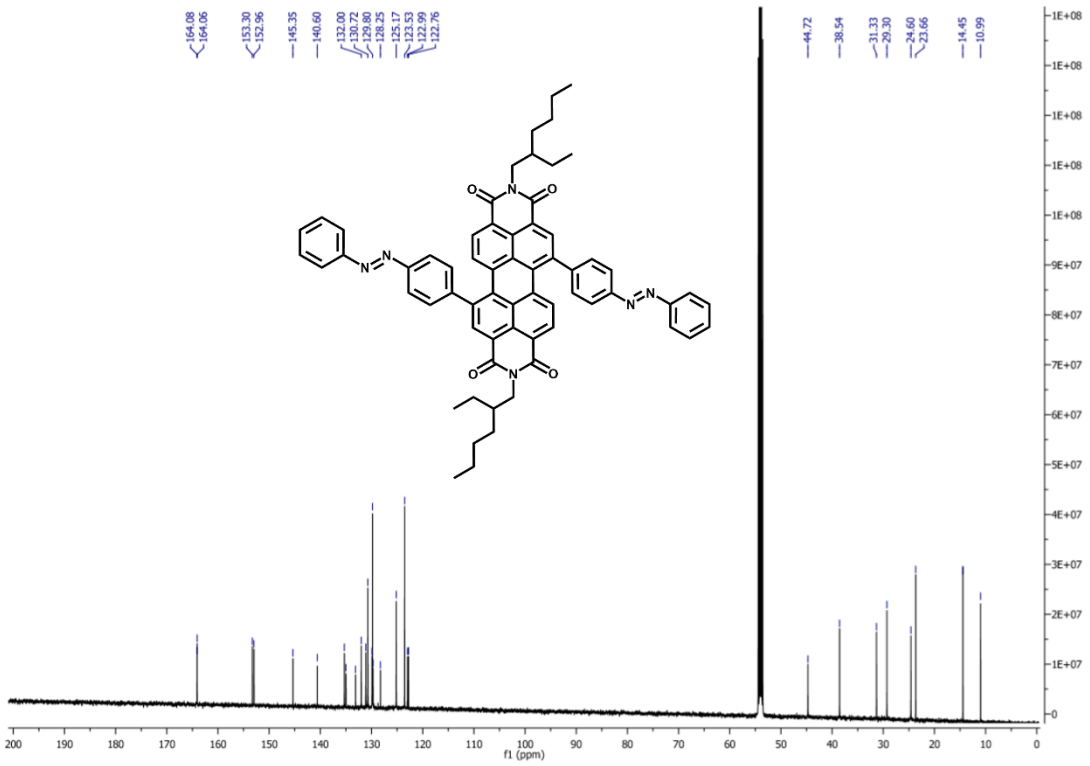
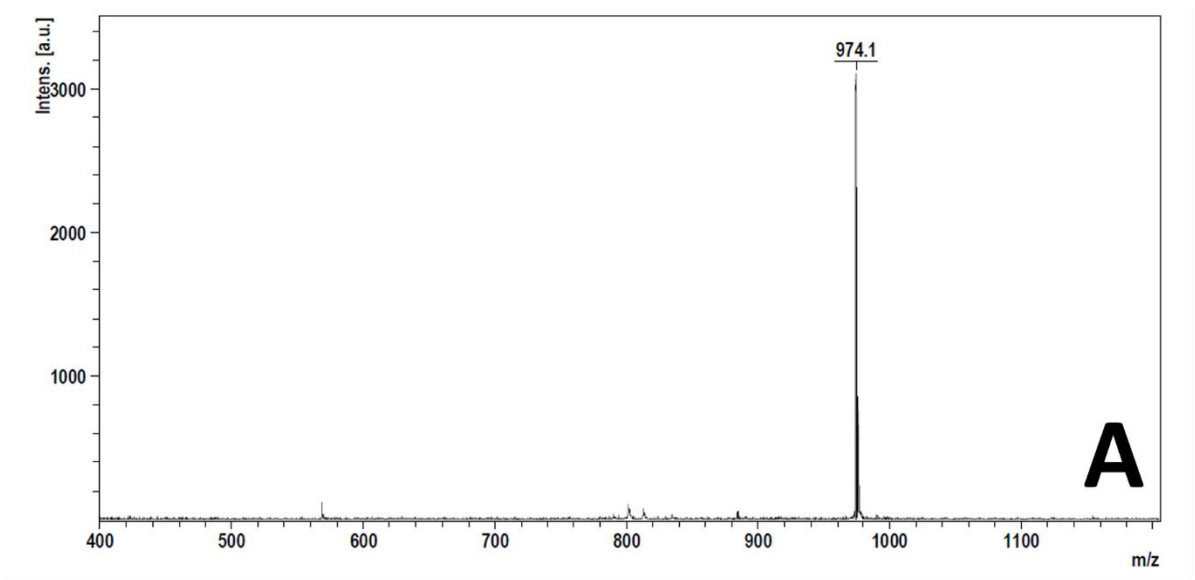


Figure S 17. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectra of **(5)** in CD_2Cl_2.



Acquisition Parameter

Source Type	APCI	Ion Polarity	Negative	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	3500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	2500 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
974.4521	1	C 64 H 58 N 6 O 4	974.4525	0.4	39.0	odd	ok

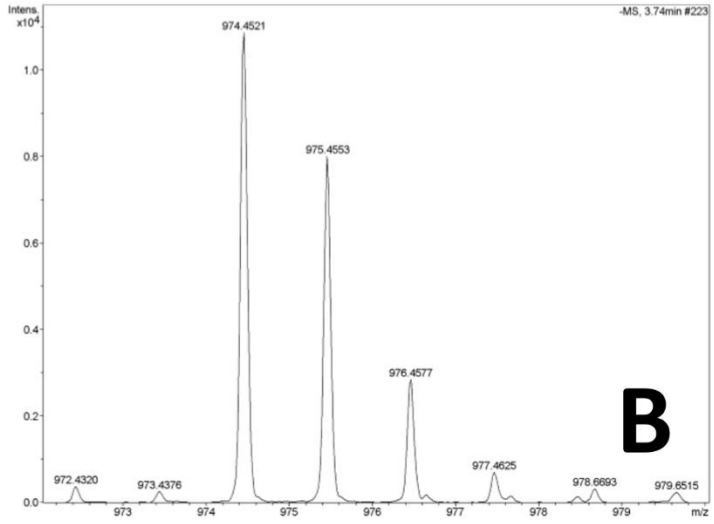


Figure S 18. MS analysis of **(5)**: MALDI-TOF spectra (A) and HRMS (APCI-TOF) spectra (B) in negative ion polarity.

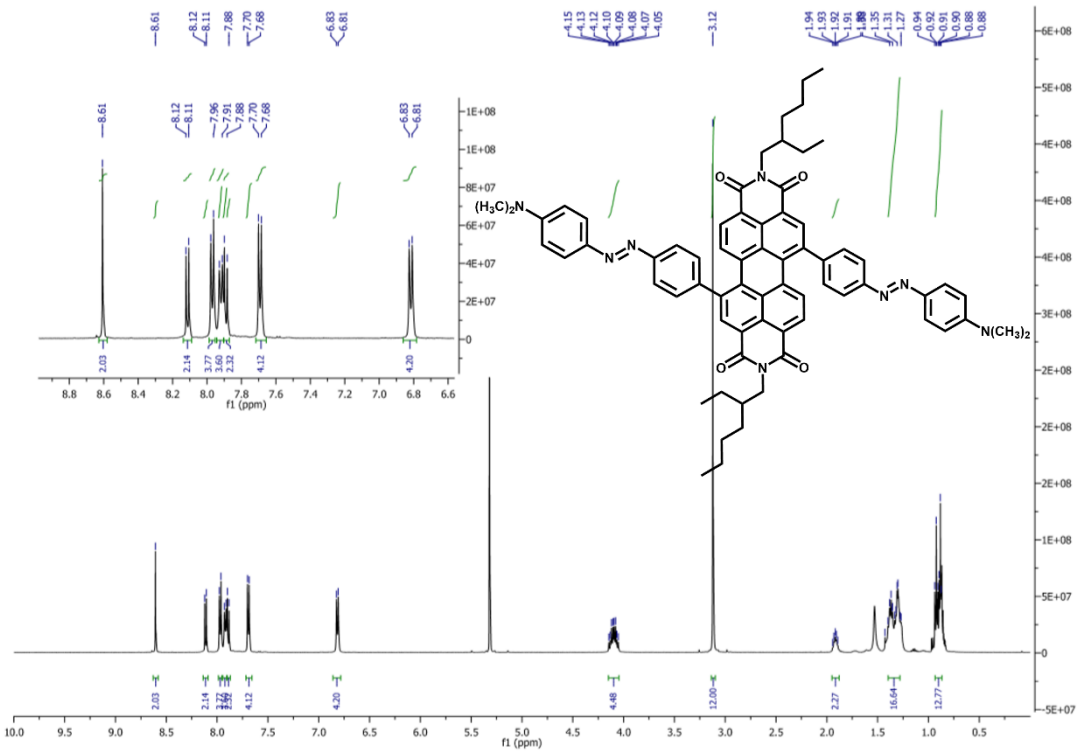


Figure S 19. ^{1}H NMR (500 MHz) spectra of **(6)** in CD_2Cl_2.

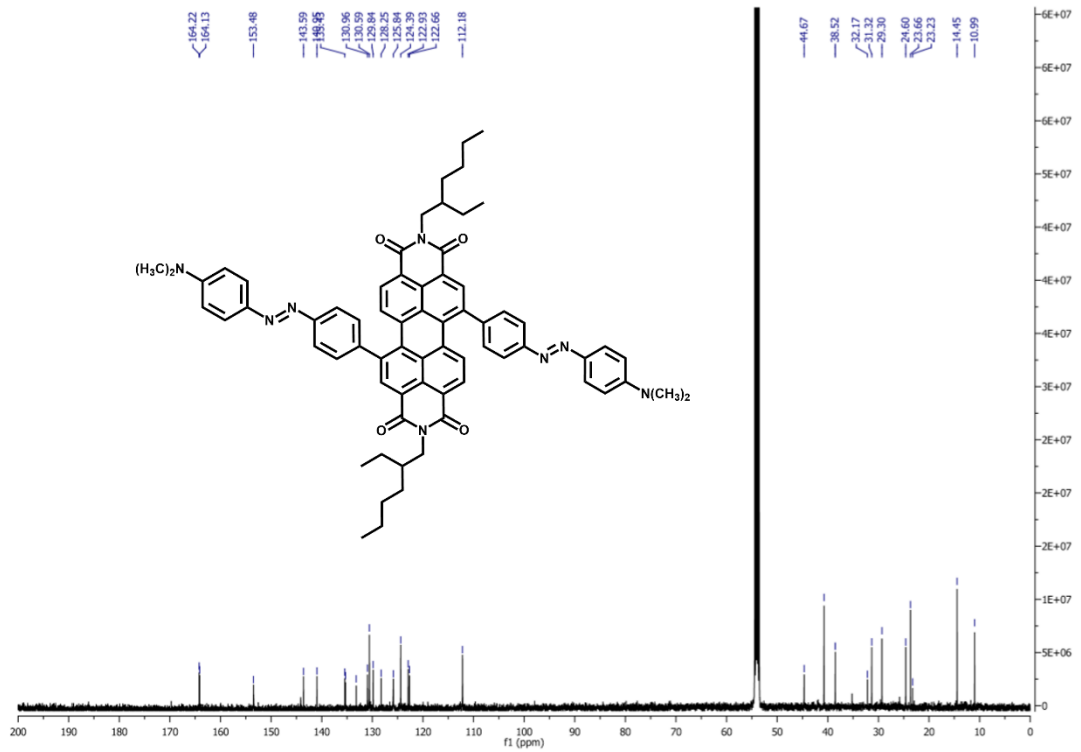
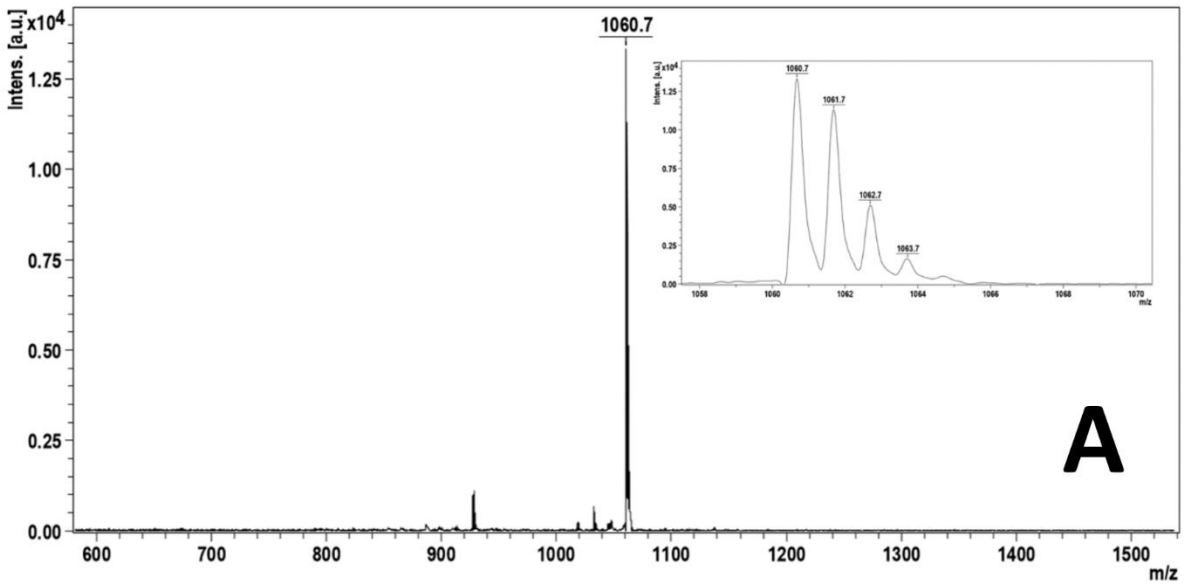


Figure S 20. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectra of **(6)** in CD_2Cl_2.



Acquisition Parameter

Source Type	APCI	Ion Polarity	Negative	Set Nebulizer	3.0 Bar
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Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	2500 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e¯ Conf	N-Rule
1060.5365	1	C 68 H 68 N 8 O 4	1060.5369	0.4	39.0	odd	ok

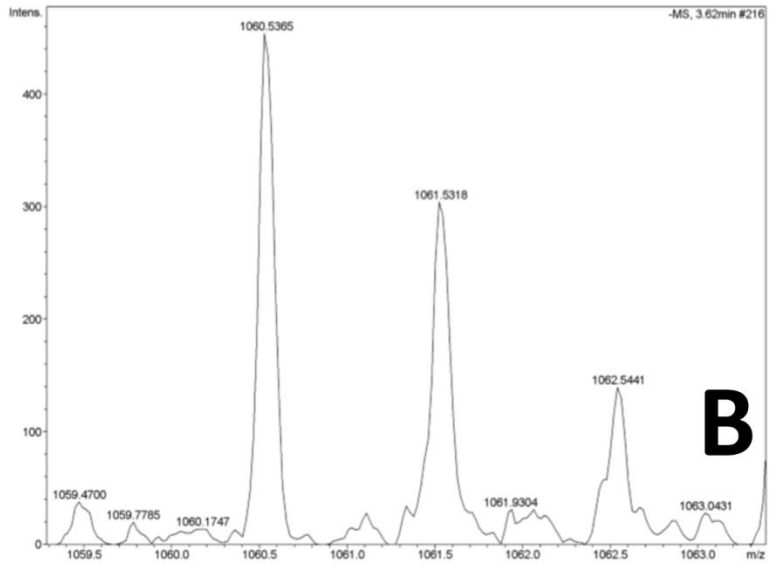


Figure S 21. MS analysis of **(6)**: MALDI-TOF spectra (A) and HRMS (APCI-TOF) spectra (B) in negative ion polarity.

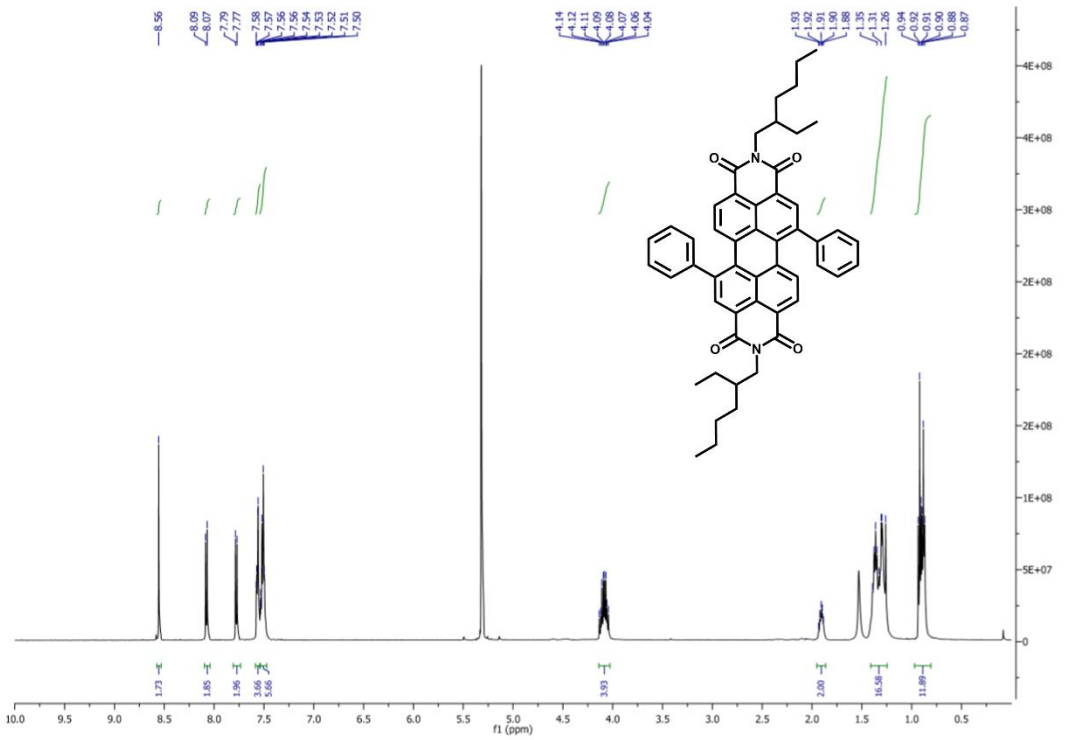


Figure S 22. ^{1}H NMR (500 MHz) spectra of model **M2** in CD_2Cl_2.

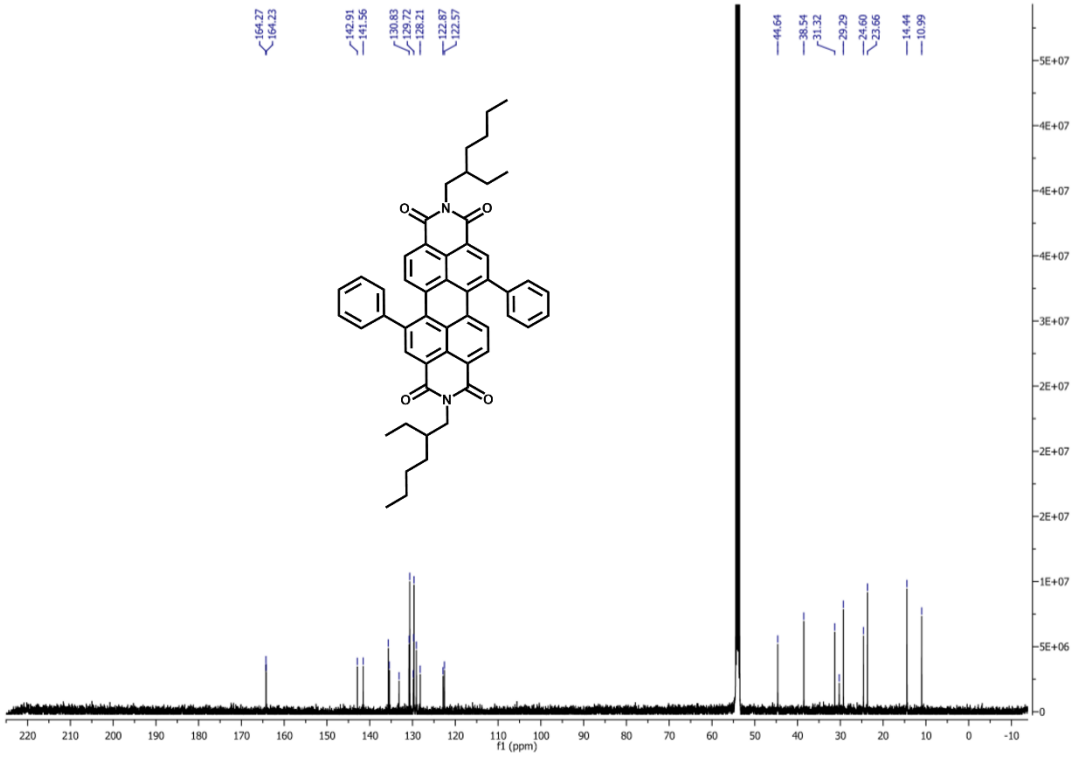
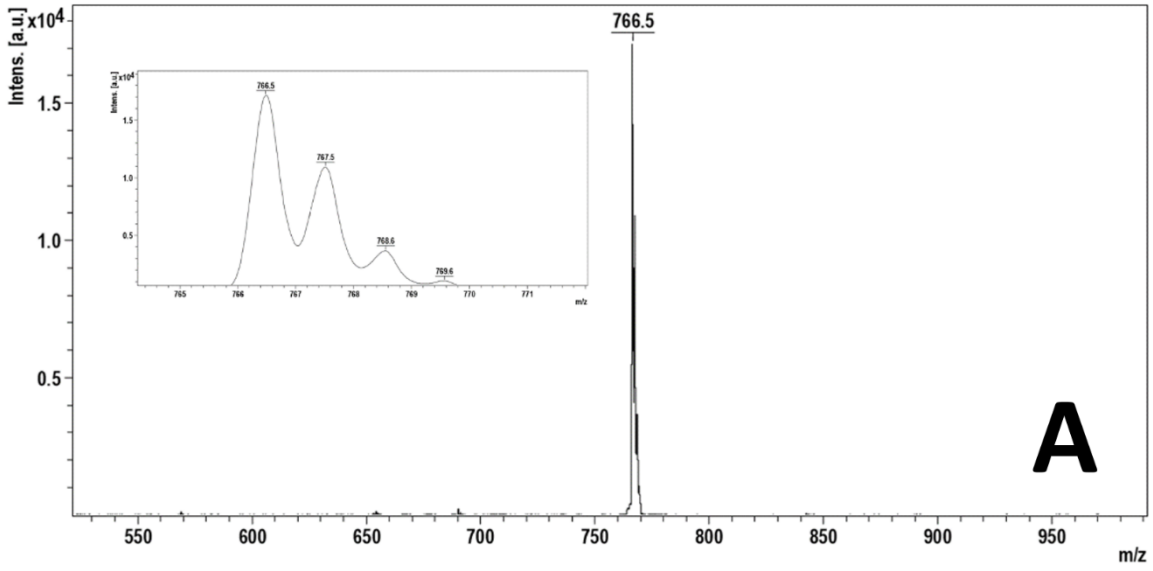


Figure S 23. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectra of model **M2** in CD_2Cl_2.



Acquisition Parameter

Source Type	APCI	Ion Polarity	Negative	Set Nebulizer	3.0 Bar
Focus	Not active	Set Capillary	3500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	2500 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	rdb	e⁻ Conf	N-Rule
766.3774	1	C 52 H 50 N 2 O 4	766.3776	0.2	29.0	odd	ok

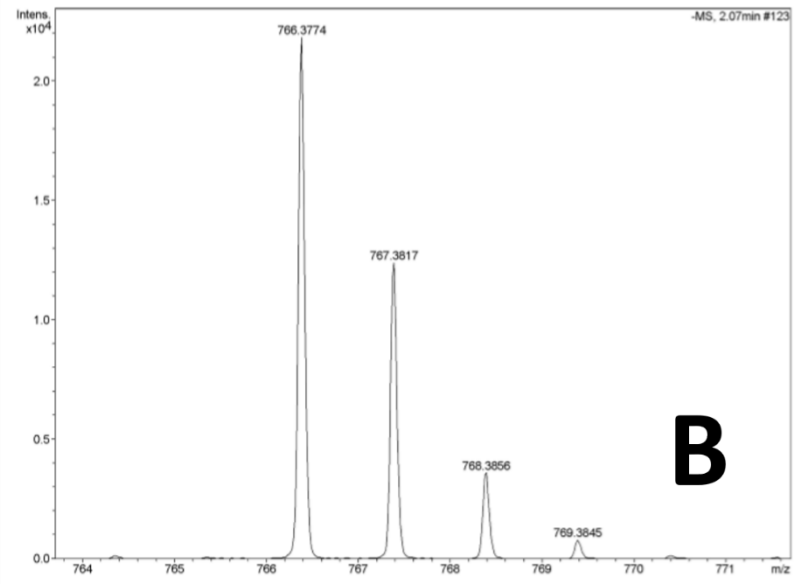


Figure S 24. MS analysis of **M_2**: MALDI-TOF spectra (A) and HRMS (APCI-TOF) spectra (B) in negative ion polarity.

2. 3D Architectures and Frontier Orbitals of Azo-PBIs Obtained by DFT

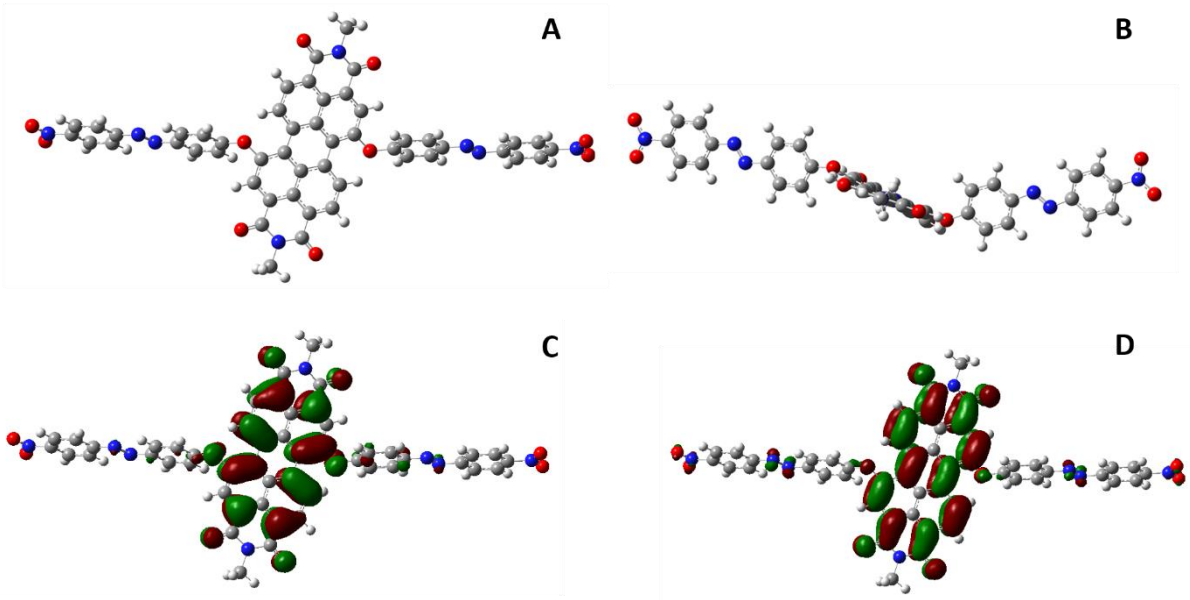


Figure S 25. 3D structures (Side view (A), top view (B)) and frontier orbitals HOMO (C), LUMO (D)) of the lowest energy conformers of **(1)** obtained by DFT using B3LYP/6-31G(d) basis set.

Table S 1. Symbolic Z- Matrix of **(1)**, Charge:0, Multiplicity:1.

C	2.58843	0.62155	-0.1271
C	1.31532	0.21081	0.32917
C	0.4009	1.25244	0.72601
C	0.82641	2.62271	0.71495
C	2.11862	2.96009	0.24182
C	2.97264	1.9681	-0.1915
C	-0.9428	0.96003	1.15512
C	-0.0266	3.65924	1.17354
H	3.94567	2.24821	-0.5751
C	-1.2849	3.34004	1.65476
C	-1.7322	2.01434	1.64356
H	-1.9201	4.13376	2.02954
H	-2.7179	1.8013	2.01849
C	0.87705	-1.1913	0.44393
C	-0.4925	-1.4751	0.79534
C	1.73998	-2.2776	0.22061
C	-1.4336	-0.4239	1.08713
C	-0.9209	-2.8442	0.83379
C	1.31393	-3.6068	0.31252

H	2.76361	-2.089	-0.0469
C	-2.7779	-0.8055	1.28729
C	-2.2765	-3.1584	1.10652
C	-0.0071	-3.9033	0.60165
H	2.00839	-4.421	0.14259
C	-3.1888	-2.1452	1.31362
H	-4.2228	-2.4003	1.51081
O	3.48501	-0.3354	-0.6254
O	-3.7546	0.16964	1.55287
C	0.40537	5.07208	1.15866
O	-0.3294	5.99564	1.56929
C	2.57578	4.36462	0.19245
O	3.70584	4.68571	-0.2364
C	-0.4358	-5.3157	0.6613
O	0.36009	-6.26	0.46972
C	-2.7419	-4.5596	1.1674
O	-3.9327	-4.8599	1.40342
N	1.6905	5.34339	0.65484
N	-1.7911	-5.5613	0.94588
C	2.15523	6.74294	0.60842
H	2.42004	7.00783	-0.4173
H	1.34632	7.37172	0.97275
H	3.04323	6.85936	1.23404
C	-2.2616	-6.958	1.01419
H	-1.4062	-7.6038	0.8305
H	-2.6893	-7.1546	1.99966
H	-3.0374	-7.1238	0.26332
C	-5.0394	0.10353	0.98491
C	-6.0866	0.5939	1.77909
C	-5.2601	-0.3457	-0.3225
C	-7.3758	0.63086	1.26221
H	-5.8697	0.93123	2.78556
C	-6.5573	-0.3102	-0.8318
H	-4.4382	-0.708	-0.9275
C	-7.6184	0.17457	-0.0494
H	-8.2061	0.99957	1.85084
H	-6.7731	-0.6474	-1.8388
C	4.88148	-0.1933	-0.5249
C	5.62415	-0.6101	-1.6388
C	5.50438	0.24497	0.6498
C	7.01269	-0.579	-1.5832
H	5.09872	-0.9466	-2.5244
C	6.89721	0.27772	0.69608

H	4.91466	0.54982	1.5057
C	7.65707	-0.1303	-0.4128
H	7.61551	-0.8892	-2.4272
H	7.42093	0.61082	1.5843
N	-8.8915	0.16316	-0.6711
N	-9.863	0.6056	0.0345
N	9.06328	-0.0524	-0.2516
N	9.7628	-0.4191	-1.2581
C	11.1735	-0.3335	-1.0837
C	11.9414	-0.7376	-2.1887
C	11.8023	0.1186	0.09346
C	13.3323	-0.6951	-2.1297
H	11.4258	-1.079	-3.078
C	13.1898	0.1643	0.16077
H	11.1896	0.42525	0.93112
C	13.9362	-0.2438	-0.9529
H	13.9493	-0.9997	-2.9642
H	13.7054	0.50628	1.04837
C	-11.137	0.58596	-0.6016
C	-11.363	0.12114	-1.9124
C	-12.203	1.07179	0.17349
C	-12.649	0.14369	-2.44
H	-10.526	-0.2485	-2.4902
C	-13.495	1.09793	-0.3475
H	-11.994	1.42098	1.17727
C	-13.698	0.6321	-1.6494
H	-12.859	-0.2055	-3.4423
H	-14.335	1.4658	0.22593
N	-15.052	0.65507	-2.2057
O	-15.987	1.10033	-1.4789
O	-15.219	0.22842	-3.385
N	15.3983	-0.1958	-0.8816
O	15.9286	0.21576	0.19062
O	16.0563	-0.5684	-1.8957

Table S 2. Summary of optimization of **(1)**.

File Name	**(1)**
File Type	.log
Calculation Type	FOPT
Calculation Method	RB3LYP
Basis Set	6-31G
Charge	0
Spin	Singlet
E(RB3LYP)	-3111.2 Hartree
RMS Gradient Norm	0.016694 Hartree/Bohr
Imaginary Freq	64
Dipole Moment	2.1603 Debye
Point Group	C1

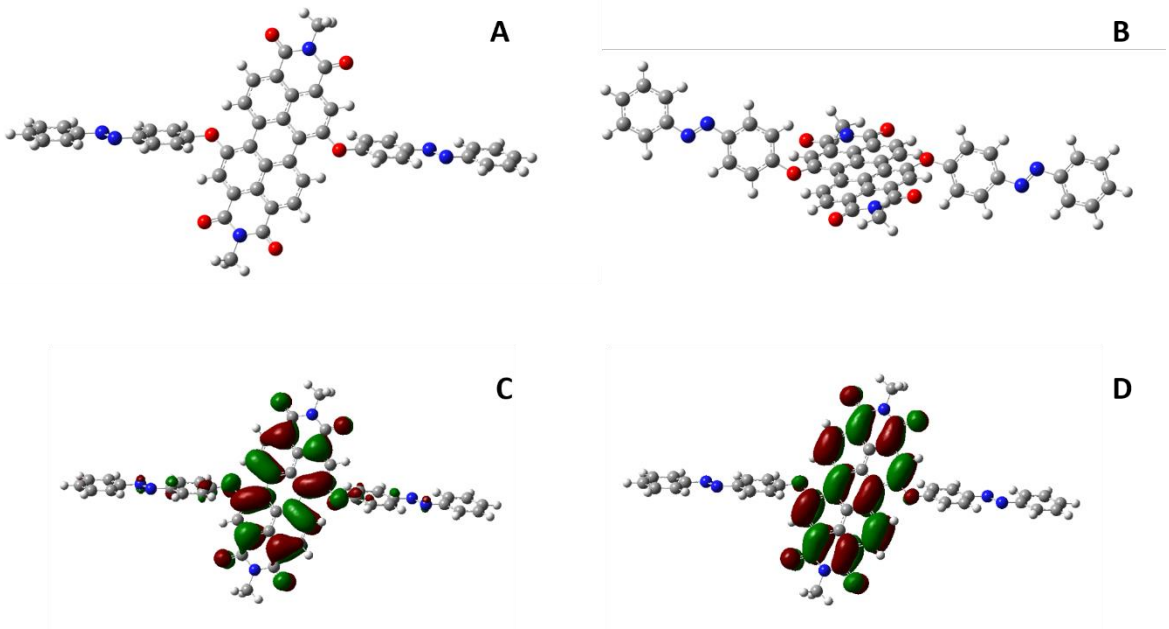


Figure S 26. 3D structures (Side view (A), top view (B)) and frontier orbitals HOMO (C), LUMO (D)) of the lowest energy conformers of **(2)** obtained by DFT using B3LYP/6-31G(d) basis set.

Table S 3. Symbolic Z- Matrix of **(2)**, Charge:0, Multiplicity:1.

C	-3.70207	-1.08254	-0.04639
C	-2.30309	-1.03049	-0.01741
C	-1.65378	0.19926	0.14094
C	-2.39976	1.38048	0.24288
C	-3.79449	1.33395	0.18383
C	-4.44734	0.10075	0.05848
H	-4.20107	-2.02264	-0.14931

C	-0.25801	0.24732	0.20303
C	-1.75097	2.60392	0.42693
H	-5.51561	0.06193	0.03835
C	-0.35661	2.64672	0.53151
C	0.39169	1.46898	0.396
H	0.13529	3.57966	0.70918
C	-1.47723	-2.32385	-0.15645
C	-0.0799	-2.27623	-0.0908
C	-2.12284	-3.5477	-0.35805
C	0.56776	-1.04612	0.07121
C	0.67153	-3.45724	-0.19438
C	-1.37067	-4.72694	-0.48448
C	1.96599	-0.9899	0.10881
C	2.06722	-3.40549	-0.13803
C	0.02658	-4.68343	-0.38143
H	-1.86267	-5.66206	-0.65437
C	2.71576	-2.1688	-0.00311
H	2.46132	-0.04668	0.22434
H	3.78441	-2.12518	0.0161
C	-2.56031	3.90882	0.52086
O	-1.99404	4.96016	0.91212
C	-4.62184	2.62896	0.26182
O	-5.86767	2.55598	0.41548
C	0.84117	-5.98728	-0.48188
O	0.2736	-7.04203	-0.86992
C	2.89889	-4.70132	-0.23308
O	4.14311	-4.62815	-0.39847
O	1.8189	1.50794	0.45336
O	-3.54781	-3.5915	-0.43799
C	2.27338	2.82904	0.15874
C	2.47647	3.71467	1.21772
C	2.51711	3.24269	-1.16317
C	2.9248	5.01176	0.97073
H	2.28933	3.39641	2.2196
C	2.96603	4.55226	-1.413
H	2.36218	2.56504	-1.97637
C	3.17021	5.43187	-0.34001
H	3.07942	5.68594	1.78603
H	3.15207	4.87937	-2.4175
C	-3.99608	-4.91663	-0.15496
C	-4.16676	-5.80954	-1.21776
C	-4.26213	-5.32577	1.15991
C	-4.60456	-7.11138	-0.97387
H	-3.96055	-5.49303	-2.21741
C	-4.70179	-6.63627	1.40486
H	-4.13018	-4.64173	1.97352

C	-4.87135	-7.52503	0.33408
H	-4.73623	-7.79217	-1.7868
H	-4.90756	-6.9563	2.40685
N	-3.98303	3.95134	0.14513
N	2.26906	-6.02761	-0.12219
C	-4.68432	4.8992	1.0209
H	-4.23689	5.86808	0.92841
H	-5.7147	4.95253	0.73667
H	-4.61005	4.56693	2.03601
C	2.38349	-6.47431	1.27429
H	3.41672	-6.5209	1.54787
H	1.87528	-5.78444	1.91563
H	1.94339	-7.44423	1.37355
N	3.64058	6.79937	-0.56675
N	-5.33079	-8.89766	0.5598
N	-5.50416	-9.63629	-0.41007
N	3.83398	7.53512	0.40102
C	4.26439	8.92228	0.2039
C	4.44088	9.42463	-1.0886
C	4.4973	9.74231	1.31481
C	4.84828	10.75033	-1.27333
H	4.26411	8.79661	-1.93442
C	4.90654	11.06859	1.13355
H	4.3623	9.35383	2.30273
C	5.08173	11.57281	-0.16264
H	4.98097	11.13448	-2.26245
H	5.08451	11.69562	1.98331
H	5.39369	12.58489	-0.30358
C	-5.95528	-11.0188	-0.22093
C	-6.1704	-11.8342	-1.33847
C	-6.16969	-11.5212	1.0668
C	-6.60484	-13.1533	-1.17137
H	-6.00283	-11.4474	-2.32114
C	-6.60266	-12.8421	1.23726
H	-6.00396	-10.8981	1.91812
C	-6.81959	-13.6581	0.11764
H	-6.77197	-13.7749	-2.02626
H	-6.76668	-13.2275	2.22151
H	-7.14952	-14.6659	0.24759

Table S 4. Summary of optimization of **(2)**.

File Name	**(2)**
File Type	.log
Calculation Type	FOPT
Calculation Method	RB3LYP
Basis Set	6-31G
Charge	0
Spin	Singlet
E(RB3LYP)	-2702.37 Hartree
RMS Gradient Norm	0.016489Hartree/Bohr
Imaginary Freq	59
Dipole Moment	2.917 Debye
Point Group	C1

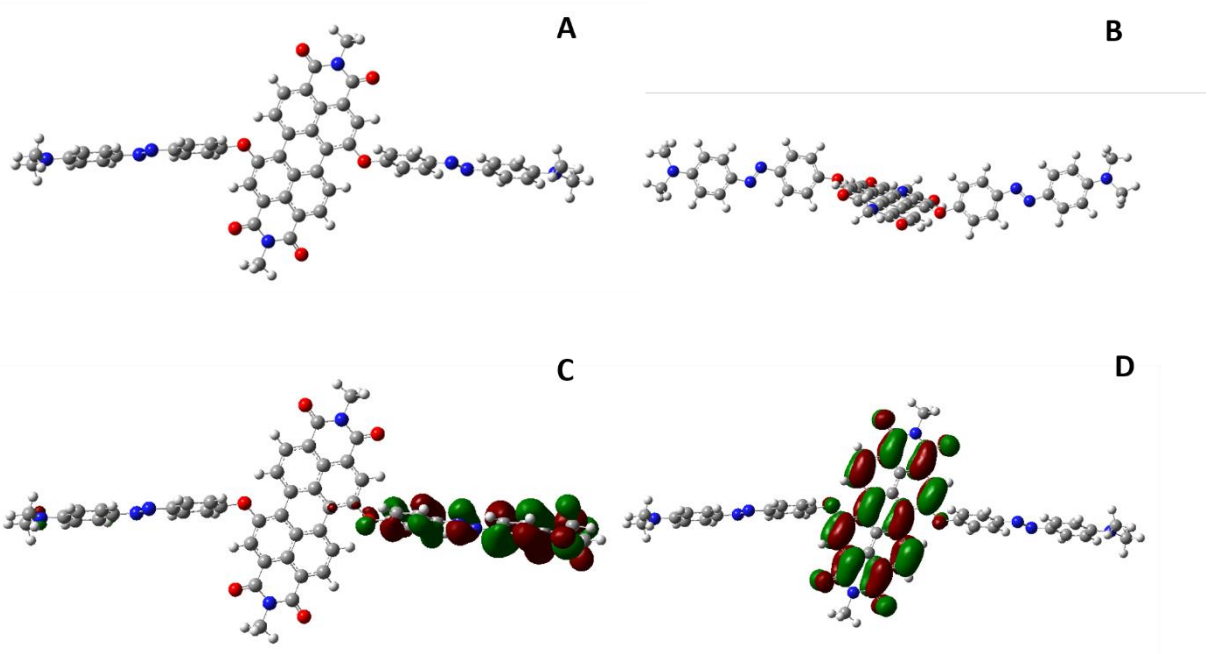


Figure S 27. 3D structures (Side view (A), top view (B)) and frontier orbitals HOMO (C), LUMO (D)) of the lowest energy conformers of **(3)** obtained by DFT using B3LYP/6-31G(d) basis set.

Table S 5. Symbolic Z-Matrix of **(3)**, Charge: 0, Multiplicity: 1.

C	-6.1712	-0.05132	0.5777
C	-4.79868	0.00181	0.30132
C	-4.21406	1.20875	-0.10964
C	-4.9962	2.36899	-0.20966
C	-6.36188	2.31991	0.08662
C	-6.95391	1.1052	0.46132
H	-6.62113	-0.97461	0.87768
C	-2.84958	1.25419	-0.42579

C	-4.41596	3.57072	-0.62833
H	-8.00418	1.06216	0.66265
C	-3.05898	3.60891	-0.9765
C	-2.27403	2.45246	-0.87065
H	-2.6213	4.52259	-1.32053
C	-3.93318	-1.26469	0.44646
C	-2.56827	-1.21866	0.13033
C	-4.50481	-2.46219	0.90196
C	-1.98503	-0.01253	-0.28574
C	-1.78375	-2.37533	0.23917
C	-3.71395	-3.61254	1.0222
C	-0.61387	0.04098	-0.56841
C	-0.41968	-2.32524	-0.06091
C	-2.35866	-3.57447	0.67051
H	-4.1468	-4.52334	1.37917
C	0.16983	-1.11323	-0.44428
H	-0.16474	0.96246	-0.87728
H	1.21965	-1.07124	-0.6459
C	-5.26038	4.85486	-0.71684
O	-4.78602	5.86734	-1.29505
N	-6.60758	4.92494	-0.126
C	0.4459	-3.59427	0.0333
O	1.69914	-3.48958	-0.02049
N	-0.16584	-4.92913	0.17124
C	-7.45808	5.77204	-0.97205
H	-7.02644	6.74733	-1.0477
H	-7.53425	5.33904	-1.9479
H	-8.43257	5.84557	-0.53775
C	0.69233	-5.77069	1.01781
H	1.66429	-5.846	0.57736
H	0.77431	-5.33173	1.9901
H	0.26288	-6.74682	1.10229
C	-7.22406	3.59239	-0.00247
C	-1.51016	-4.85565	0.76969
O	-8.47816	3.49307	0.04251
O	-1.97854	-5.86258	1.36161
O	-0.88672	2.4953	-1.21725
O	-5.89218	-2.51685	1.24888
C	-0.36166	3.79591	-0.93755
C	-0.38966	4.79469	-1.92142
C	0.18239	4.07074	0.32404
C	0.12192	6.06941	-1.63984
H	-0.8015	4.58423	-2.88668
C	0.69298	5.3445	0.60454
H	0.20777	3.30738	1.07375
C	0.65901	6.34528	-0.37514

H	0.10176	6.83176	-2.38969
H	1.10869	5.55349	1.5682
C	-6.35404	-3.8673	1.13451
C	-6.88144	-4.34093	-0.07533
C	-6.27407	-4.72043	2.24358
C	-7.31807	-5.67088	-0.17546
H	-6.95049	-3.68928	-0.92178
C	-6.71062	-6.04797	2.14358
H	-5.87772	-4.35646	3.16908
C	-7.22826	-6.52578	0.93324
H	-7.71962	-6.03342	-1.09809
H	-6.64773	-6.69703	2.99193
N	1.18551	7.68381	-0.07061
N	1.16509	8.57278	-0.92334
N	-7.6748	-7.92345	0.8263
N	-8.11049	-8.34814	-0.24463
C	-8.53326	-9.75126	-0.3684
C	-9.01698	-10.2267	-1.59383
C	-8.45266	-10.6134	0.73479
C	-9.42192	-11.562	-1.71774
H	-9.07737	-9.56947	-2.43617
C	-8.86018	-11.9499	0.61106
H	-8.0806	-10.2524	1.67105
C	-9.34547	-12.4236	-0.61577
H	-9.79029	-11.9241	-2.65458
H	-8.80089	-12.6082	1.45283
C	1.62157	9.92386	-0.56915
C	1.62122	10.94461	-1.53013
C	2.05668	10.18913	0.73565
C	2.05481	12.2319	-1.18305
H	1.29054	10.74195	-2.52766
C	2.48937	11.47558	1.0821
H	2.05819	9.40821	1.46789
C	2.48917	12.49699	0.12289
H	2.05441	13.01237	-1.91412
H	2.82002	11.67803	2.07909
N	-9.77542	-13.8234	-0.74966
N	2.945	13.84602	0.48773
C	2.66188	14.09168	1.90916
H	3.17512	13.36641	2.50558
H	2.99601	15.07274	2.17474
H	1.60883	14.0145	2.08197
C	4.39161	13.95456	0.25278
H	4.59987	13.77266	-0.78076
H	4.72331	14.93734	0.5159
H	4.90504	13.23236	0.85269

C	-11.2083	-13.9256	-0.43819
H	-11.524	-14.9428	-0.53951
H	-11.3792	-13.5972	0.56554
H	-11.7645	-13.3104	-1.11438
C	-9.00958	-14.6645	0.18157
H	-9.32442	-15.6825	0.08409
H	-7.96675	-14.5905	-0.04585
H	-9.1802	-14.3332	1.18459

Table S 6. Summary of optimization of **(3)**.

File Name	**(3)**
File Type	.log
Calculation Type	FOPT
Calculation Method	RB3LYP
Basis Set	6-31G
Charge	0
Spin	Singlet
E(RB3LYP)	-2970.41 Hartree
RMS Gradient Norm	1.48E-06 Hartree/Bohr
Imaginary Freq	56
Dipole Moment	2.6516 Debye
Point Group	C1

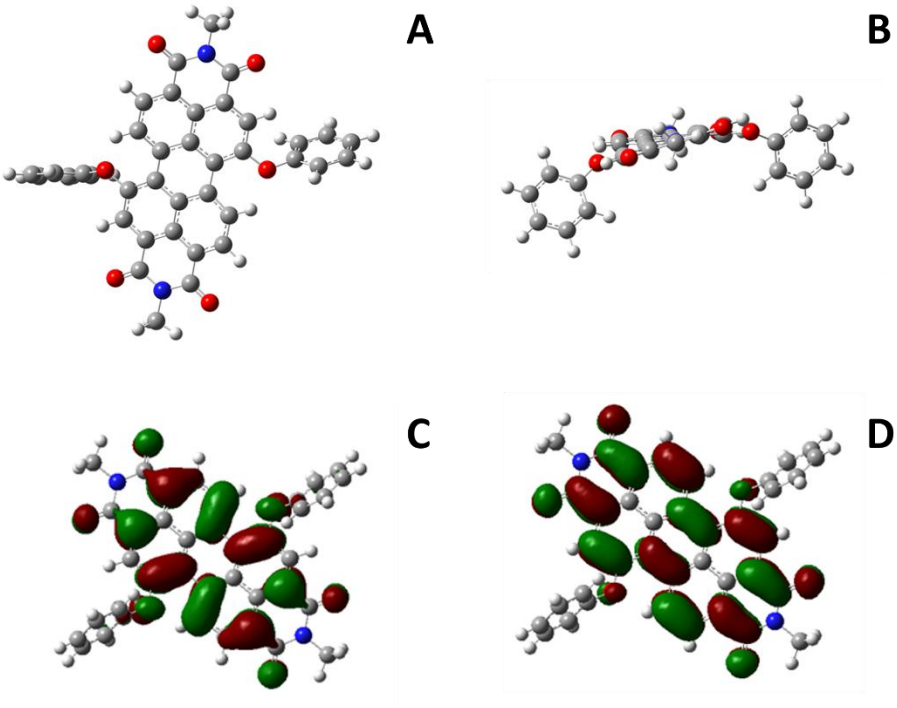


Figure S 28. 3D structures (Side view (A), top view (B)) and Frontier orbitals HOMO (C), LUMO (D)) of the lowest energy conformers of **(M_1)** obtained by DFT using B3LYP/6-31G(d) basis set.

Table S 7. Symbolic Z-Matrix of **M_1**, Charge:0, Multiplicity:1.

C	-4.24442	0.06288	0.44298
C	-1.83552	-0.21753	0.44547
C	-1.69036	1.16984	0.40029
C	-2.82129	1.98471	0.35477
C	-0.69948	-1.03727	0.44368
C	-0.41902	1.74536	0.40775
C	0.71615	0.92685	0.3818
C	0.57197	-0.46226	0.39798
C	-0.29559	3.13702	0.44483
C	-1.44449	3.94128	0.42323
H	-1.34687	5.00683	0.46472
H	-5.2262	-0.36304	0.48025
C	-0.82373	-2.4285	0.48679
C	0.32281	-3.2329	0.42974
C	1.55736	-2.67128	0.36819
C	1.70264	-1.27894	0.3609
H	0.22335	-4.29809	0.43539
C	3.12037	0.64801	0.27317
H	4.09845	1.07689	0.21704
C	2.97544	-0.70379	0.28835
O	-2.1128	-3.03605	0.59028

O	0.99779	3.7422	0.50746
C	-2.02839	-4.38392	0.12153
C	-1.75517	-5.41621	1.03023
C	-2.21312	-4.67588	-1.23537
C	-1.66363	-6.74005	0.58429
H	-1.61651	-5.1922	2.06689
C	-2.11913	-6.00104	-1.68313
H	-2.42441	-3.88931	-1.92893
C	-1.84223	-7.03212	-0.77334
H	-1.45703	-7.52784	1.28062
H	-2.25881	-6.22641	-2.71952
H	-1.76635	-8.04297	-1.11585
C	0.91087	5.10251	0.07582
C	0.6415	6.0989	1.02254
C	1.09098	5.44622	-1.27185
C	0.55373	7.43989	0.62786
H	0.50337	5.8346	2.05044
C	1.00362	6.79012	-1.66725
H	1.29508	4.68757	-1.9971
C	0.73492	7.7862	-0.71754
H	0.34777	8.19945	1.35414
H	1.14193	7.05523	-2.69317
H	0.66836	8.81001	-1.01946
C	4.22442	-1.59817	0.21355
O	5.33157	-1.07998	-0.08066
C	1.9965	1.48548	0.3329
H	2.11815	2.54867	0.33897
C	-3.11863	-0.77394	0.49063
H	-3.24187	-1.83398	0.56053
C	-4.09693	1.40939	0.34428
C	-2.67919	3.37756	0.34127
C	-3.92007	4.28227	0.23917
O	-3.80333	5.51811	0.44833
C	2.79545	-3.58089	0.29765
O	2.64502	-4.81152	0.08159
N	4.15272	-3.04478	0.48998
C	5.07112	-3.75071	-0.41629
H	5.03367	-4.79986	-0.21304
H	4.77525	-3.5731	-1.43048
H	6.06815	-3.39277	-0.26722
N	-5.23982	3.72841	-0.11515
C	-6.28527	4.47085	0.60351
H	-6.22097	5.50947	0.35263
H	-7.24577	4.09273	0.32225
H	-6.14952	4.34952	1.65714
C	-5.3467	2.29938	0.22975

O	-6.48261	1.79351	0.42166

Table S 8. Summary of optimization of **M_1**.

File Name	**M_1**
File Type	.log
Calculation Type	FOPT
Calculation Method	RB3LYP
Basis Set	6-31G
Charge	0
Spin	Singlet
E(RB3LYP)	-2021.72 Hartree
RMS Gradient Norm	1.39E-06 Hartree/Bohr
Imaginary Freq	56
Dipole Moment	2.2575 Debye
Point Group	C1

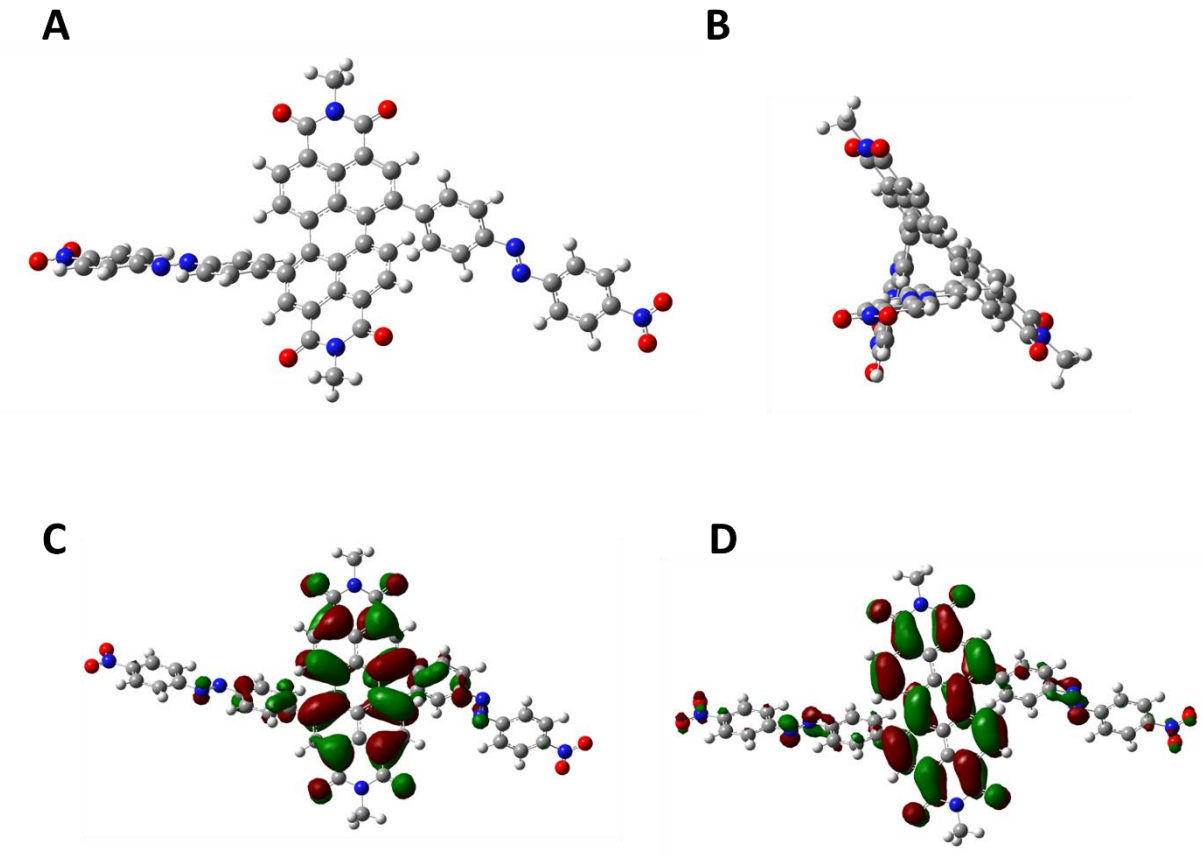


Figure S 29. 3D structures (Side view (A), top view (B)) and frontier orbitals HOMO (C), LUMO (D)) of the lowest energy conformers of **(4)** obtained by DFT using B3LYP/6-31G(d) basis set.

Table S 9. Symbolic Z-Matrix of **(4)**, Charge:0, Multiplicity:1.

C	-2.74159	-0.33831	0.10756
C	-2.05961	1.56258	-0.10755
C	-2.77887	2.76532	-0.10741
C	-4.1801	2.7438	-0.10728
C	-4.86208	1.51953	-0.10729
C	-0.65838	1.5841	-0.10768
C	-2.09689	3.98959	-0.1074
H	-5.93195	1.5031	-0.10719
C	-0.69566	4.01111	-0.10752
C	0.0236	2.80837	-0.10766
H	-0.17495	4.94587	-0.10751
C	-1.95119	-0.98338	-0.10772
C	-0.54996	-0.96186	-0.10785
C	-2.63317	-2.20765	-0.10773
C	0.13202	0.26241	-0.10783
C	0.1693	-2.1646	-0.10799
C	-1.91391	-3.41039	-0.10787
C	1.57053	-2.14308	-0.10812
C	-0.51268	-3.38887	-0.108
H	-2.43462	-4.34515	-0.10788
C	2.25251	-0.91881	-0.10811
H	3.32238	-0.90237	-0.10821
C	-2.88729	5.31128	-0.10724
O	-2.3321	6.40585	-0.10722
C	-4.9705	4.06549	-0.10712
O	-6.19748	4.0943	-0.10701
C	2.36093	-3.46477	-0.10827
O	3.58791	-3.49358	-0.10839
C	0.27772	-4.71056	-0.10816
O	-0.27747	-5.80513	-0.10818
N	1.54809	-4.68959	-0.10822
N	-4.15766	5.29032	-0.10707
C	-4.46215	6.08052	-1.30864
H	-5.50766	6.0114	-1.5255
H	-4.20011	7.10387	-1.13838
H	-3.90033	5.70149	-2.13663
C	1.85481	-5.48118	1.09186
H	1.59212	-6.50427	0.92105
H	2.90079	-5.4126	1.30665
H	1.2948	-5.10287	1.92142
C	-4.17299	-2.2313	-0.10758
C	-4.87038	-2.23756	1.10075
C	-4.87046	-2.24636	-1.31541
C	-6.26492	-2.25955	1.10116
H	-4.3202	-2.22646	2.05282

C	-6.26544	-2.26737	-1.31518
H	-4.32097	-2.24126	-2.26786
C	-6.96272	-2.2741	-0.10717
H	-6.81467	-2.26511	2.05355
H	-6.8151	-2.27882	-2.26766
C	1.56342	2.83202	-0.1078
C	2.26086	2.84987	1.10039
C	2.26085	2.8355	-1.31575
C	3.6554	2.87187	1.10054
H	1.71071	2.84791	2.05254
C	3.65583	2.8565	-1.31576
H	1.71132	2.82125	-2.26808
C	4.35316	2.87482	-0.1079
H	4.20518	2.88657	2.05281
H	4.20546	2.85882	-2.26833
N	5.82297	2.89793	-0.10741
N	6.42213	3.97441	-0.11167
N	-8.43254	-2.2972	-0.1064
N	-9.0317	-3.37369	-0.10514
C	7.89195	3.99751	-0.1113
C	8.58885	4.02313	1.09706
C	8.5899	3.99372	-1.31894
C	9.98338	4.04562	1.09768
H	8.03829	4.02689	2.04896
C	9.98488	4.01522	-1.31848
H	8.0408	3.97336	-2.27141
C	10.68167	4.04131	-0.11045
H	10.53274	4.06644	2.05008
H	10.53492	4.01181	-2.2708
C	-10.5015	-3.39678	-0.10114
C	-11.1958	-3.40044	1.109
C	-11.2021	-3.41493	-1.30713
C	-12.5903	-3.42293	1.11307
H	-10.6432	-3.38691	2.05961
C	-12.5971	-3.43643	-1.30324
H	-10.6551	-3.41187	-2.261
C	-13.2912	-3.44057	-0.09342
H	-13.1376	-3.42645	2.06689
H	-13.1492	-3.45032	-2.25426
N	-14.761	-3.46418	-0.08879
O	-15.3482	-2.41843	-0.09178
O	-15.3143	-4.52826	-0.08222
N	12.15148	4.06494	-0.10946
O	12.73867	3.01926	-0.09664
O	12.70475	5.12897	-0.12152
C	-4.14282	0.31679	-0.10743

H	-4.66353	-0.61797	-0.10744
C	1.53325	0.28393	-0.10796
H	2.05396	1.21869	-0.10795

Table S 10. Summary of optimization of **(4)**.

File Name	**(4)**
File Type	.log
Calculation Type	FOPT
Calculation Method	RB3LYP
Basis Set	6-31G
Charge	0
Spin	Singlet
E(RB3LYP)	-2961.01 Hartree
RMS Gradient Norm	2.18E-06 Hartree/Bohr
Imaginary Freq	42
Dipole Moment	3.5003 Debye
Point Group	C1

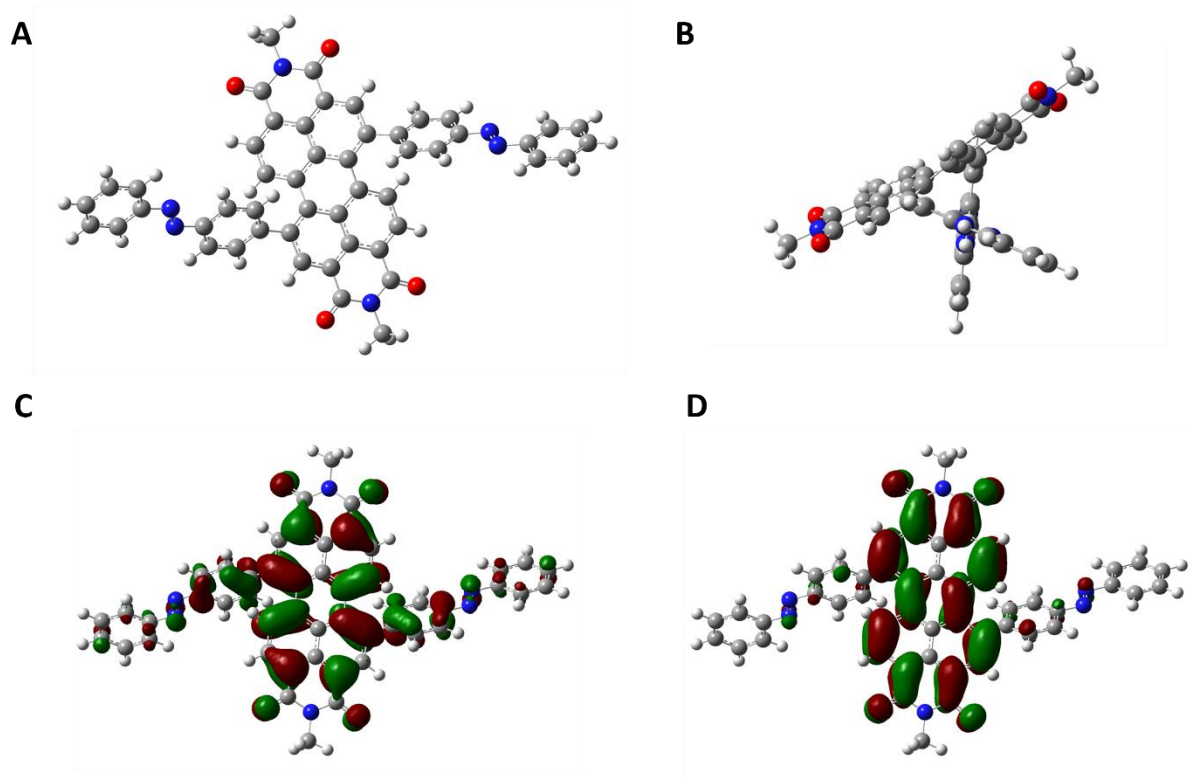


Figure S 30. 3D structures (Side view (A), top view (B)) and frontier orbitals HOMO (C), LUMO (D)) of the lowest energy conformers of **(5)** obtained by DFT using B3LYP/6-31G(d) basis set.

Table S 11. Symbolic Z-Matrix of **(5)**, Charge:0, Multiplicity:1.

C	-4.40276	-0.00935	0.00052
C	-3.00152	0.01184	0.00033
C	-2.31925	1.23594	0.00025
C	-3.03822	2.43886	0.00037
C	-4.43946	2.41767	0.00056
C	-5.12173	1.19357	0.00064
C	-0.91801	1.25713	0.00005
C	-2.35595	3.66296	0.00029
H	-6.19161	1.17739	0.00078
C	-0.95471	3.68415	0.00009
C	-0.23574	2.48123	-0.00003
H	-0.43378	4.61878	0.00003
C	-2.21145	-1.31004	0.0002
C	-0.81021	-1.28886	0.00001
C	-2.89372	-2.53415	0.00028
C	-0.12794	-0.06475	-0.00007
C	-0.09124	-2.49177	-0.0001
C	-2.17475	-3.73706	0.00017
C	1.2733	-0.04357	-0.00026
C	1.31	-2.47058	-0.0003
C	-0.77351	-3.71587	-0.00002
H	-2.69568	-4.67169	0.00023
C	1.99227	-1.24648	-0.00038
H	3.06215	-1.2303	-0.00052
C	1.30408	2.50452	-0.00024
C	1.98635	3.72862	-0.00032
C	2.02305	1.3016	-0.00036
C	3.38759	3.74981	-0.00052
H	1.4374	4.64707	-0.00023
C	3.42429	1.32279	-0.00056
C	4.10656	2.54689	-0.00064
H	3.90852	4.68444	-0.00058
H	3.97324	0.40434	-0.00065
H	0.75743	0.74623	-0.0729
H	2.40317	0.5622	-0.0587
C	-4.43354	-2.55743	0.00049
C	-5.11272	-3.77612	0.00057
C	-5.14923	-1.36021	0.00071
C	-6.50726	-3.79748	0.00019
H	-4.54819	-4.71981	-0.00038
C	-6.54421	-1.38141	0.00133
C	-7.22329	-2.59976	0.00093
H	-7.04267	-4.75802	-0.00038
H	-7.10823	-0.43729	0.00192
H	-5.64311	-0.56063	0.59891

H	-4.01182	-0.83875	0.39763
N	5.57639	2.56912	-0.00085
N	6.80825	2.58775	-0.00102
N	-8.69311	-2.62261	0.00061
N	-9.92496	-2.64176	0.00034
C	8.27809	2.60997	-0.00123
C	8.97565	2.62352	1.20695
C	8.97539	2.6174	-1.20923
C	10.3702	2.64518	1.20703
H	8.42561	2.61844	2.15914
C	10.37037	2.63807	-1.20932
H	8.42576	2.60654	-2.16155
C	11.06783	2.6521	-0.00147
H	10.92008	2.6565	2.15928
H	10.91991	2.6435	-2.16193
C	-11.3948	-2.66462	0.00001
C	-12.0924	-2.68172	1.20812
C	-12.092	-2.66909	-1.20803
C	-13.4869	-2.70398	1.20809
H	-11.5424	-2.67897	2.16034
C	-13.487	-2.69035	-1.20823
H	-11.5424	-2.65542	-2.1603
C	-14.1845	-2.70793	-0.00045
H	-14.0368	-2.7181	2.16029
H	-14.0365	-2.69345	-2.16087
C	-5.22953	3.73956	0.00069
C	-3.14603	4.98485	0.00041
C	0.01657	-5.03776	-0.00014
C	2.10008	-3.79247	-0.00042
N	1.48635	-5.01262	-0.00035
N	-4.61581	4.95971	0.00061
O	-0.59173	-6.13937	-0.00007
O	3.3584	-3.77843	-0.0006
O	-6.48786	3.72552	0.00086
O	-2.53773	6.08646	0.00034
C	-5.11779	5.64664	-1.19816
H	-6.17253	5.80101	-1.1054
H	-4.62656	6.59178	-1.29964
H	-4.91968	5.04713	-2.06201
C	1.98825	-5.69455	1.20131
H	1.49628	-6.63881	1.30725
H	3.04282	-5.8502	1.10882
H	1.79098	-5.09099	2.06253
H	12.13771	2.66816	-0.00157
H	-15.2544	-2.72445	-0.00064

Table S 12. Summary of optimization of **(5)**.

File Name	**(5)**
File Type	.log
Calculation Type	FOPT
Calculation Method	RB3LYP
Basis Set	6-31G
Charge	0
Spin	Singlet
E(RB3LYP)	-2550.68 Hartree
RMS Gradient Norm	0.051014 Hartree/Bohr
Imaginary Freq	76
Dipole Moment	4.4454 Debye
Point Group	C1

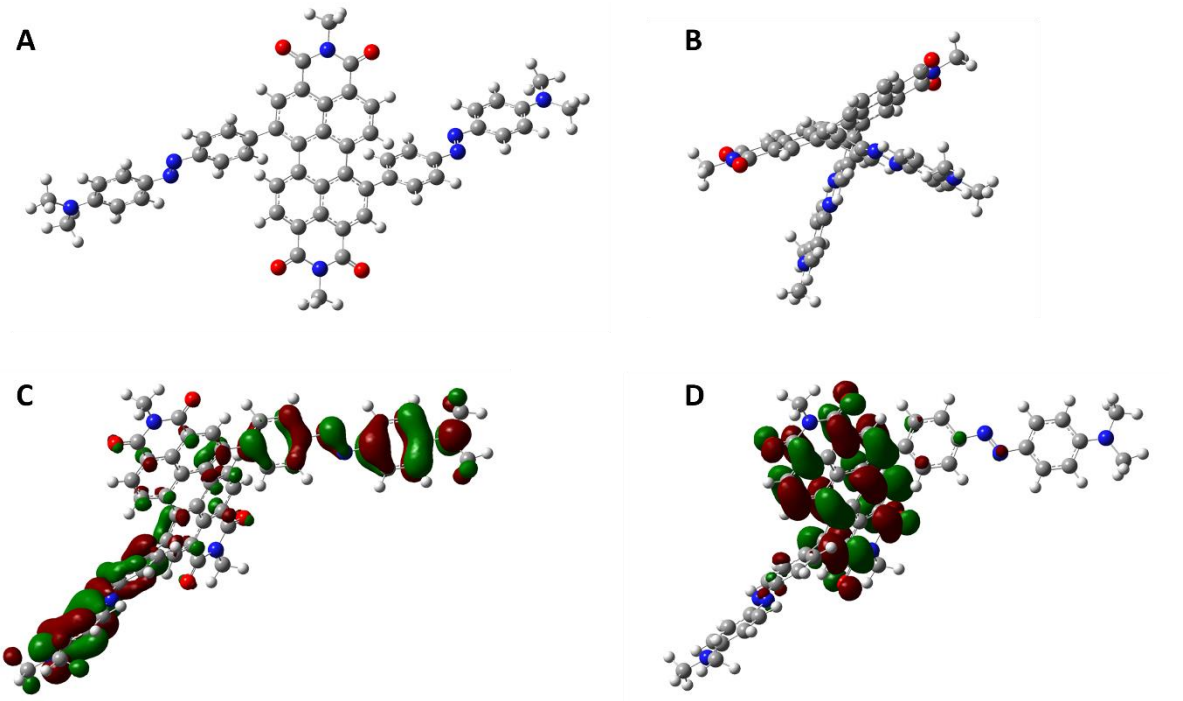


Figure S 31. 3D structures (Side view (A), top view (B)) and frontier orbitals HOMO (C), LUMO (D)) of the lowest energy conformers of **(6)** obtained by DFT using B3LYP/6-31G(d) basis set.

Table S 13. Symbolic Z-Matrix of **(6)**, Charge:0, Multiplicity:1.

C	-4.50533	0.766389	-2.2207
C	-3.13355	0.574645	-2.00357
C	-2.32224	1.723228	-1.70622
C	-2.96523	2.979346	-1.47868
C	-4.36364	3.117575	-1.66646
C	-5.11223	2.019527	-2.06711

C	-0.88935	1.636049	-1.64094
C	-2.19289	4.097328	-1.07341
H	-6.17433	2.14562	-2.24114
C	-0.83585	3.946522	-0.85309
C	-0.16125	2.728331	-1.10569
H	-0.28172	4.79281	-0.46403
C	-2.48873	-0.7451	-2.13058
C	-1.0784	-0.74696	-2.40638
C	-3.17829	-1.98285	-2.08421
C	-0.27504	0.43153	-2.22864
C	-0.45144	-1.94251	-2.87608
C	-2.51568	-3.1557	-2.51811
C	1.052577	0.406676	-2.67869
C	0.90787	-1.93307	-3.27867
C	-1.20182	-3.1434	-2.94991
H	-3.04325	-4.10236	-2.50582
C	1.634651	-0.75268	-3.2072
H	2.662505	-0.74944	-3.55034
C	1.273298	2.67915	-0.70227
C	2.172817	3.681012	-1.11581
C	1.738912	1.680595	0.184039
C	3.497446	3.672963	-0.67778
H	1.834577	4.4584	-1.79359
C	3.055178	1.673945	0.628907
C	3.950897	2.672293	0.195112
H	4.202145	4.432428	-0.99694
H	3.414146	0.916692	1.314745
H	1.654847	1.300856	-2.61867
H	1.050611	0.915418	0.528315
C	-4.54949	-2.17309	-1.53038
C	-4.8704	-1.72179	-0.22933
C	-5.52402	-2.8913	-2.25036
C	-6.12058	-1.96522	0.325944
H	-4.12133	-1.18658	0.345279
C	-6.7833	-3.1305	-1.6994
C	-7.09378	-2.67058	-0.4106
H	-6.36807	-1.62952	1.325305
H	-7.54543	-3.6729	-2.24733
H	-5.29667	-3.24917	-3.24955
H	-5.12299	-0.06975	-2.51267
N	5.314858	2.759439	0.583513
N	5.714868	1.839294	1.387817
N	-8.40127	-2.97152	0.057123
N	-8.66961	-2.5491	1.241677
C	7.060305	1.902343	1.790028
C	7.981957	2.889122	1.380032

C	7.496699	0.894461	2.668689
C	9.289555	2.866881	1.834489
H	7.643843	3.664063	0.702621
C	8.804454	0.859996	3.131552
H	6.77927	0.141293	2.975881
C	9.740664	1.849791	2.726178
H	9.972635	3.637738	1.501895
H	9.102764	0.068606	3.806193
C	-9.95627	-2.8346	1.730501
C	-10.2487	-2.37075	3.025738
C	-10.9521	-3.54124	1.023255
C	-11.4874	-2.59745	3.608675
H	-9.47546	-1.82829	3.558805
C	-12.1921	-3.77478	1.593088
H	-10.725	-3.89695	0.025461
C	-12.4973	-3.30934	2.905848
H	-11.675	-2.22471	4.606838
H	-12.935	-4.31987	1.025252
C	-5.02157	4.42062	-1.45978
C	-2.8253	5.411322	-0.83884
C	-0.58627	-4.39366	-3.43929
C	1.545603	-3.15979	-3.79051
N	0.759577	-4.3233	-3.83848
N	-4.2118	5.494621	-1.05394
O	-1.22098	-5.46979	-3.50279
O	2.735106	-3.1953	-4.17527
O	-6.24797	4.595408	-1.63186
O	-2.17027	6.410737	-0.46863
C	-4.88355	6.790636	-0.84421
H	-5.65293	6.688012	-0.07562
H	-4.12703	7.508612	-0.5363
H	-5.36559	7.110835	-1.77064
C	1.411619	-5.54482	-4.34605
H	0.678077	-6.34711	-4.31686
H	1.76223	-5.37922	-5.36726
H	2.274943	-5.78892	-3.72296
N	11.04724	1.829359	3.181
N	-13.7362	-3.54463	3.475041
C	11.99715	2.858731	2.753729
H	11.66266	3.863745	3.04339
H	12.96136	2.67381	3.228452
H	12.14571	2.848434	1.665586
C	11.4933	0.774511	4.092997
H	10.92415	0.7839	5.032261
H	11.39038	-0.22139	3.641582
H	12.54554	0.930314	4.333178

C	-14.0328	-3.05495	4.822515
H	-15.0516	-3.33726	5.089814
H	-13.3524	-3.4864	5.568985
H	-13.9553	-1.96104	4.882071
C	-14.7636	-4.28159	2.736214
H	-15.6553	-4.37098	3.357731
H	-15.0456	-3.76625	1.808222
H	-14.4275	-5.29412	2.476149

Table S 14. Summary of optimization of **(6)**.

File Name	**(6)**
File Type	.log
Calculation Type	FOPT
Calculation Method	RB3LYP
Basis Set	6-31G
Charge	0
Spin	Singlet
E(RB3LYP)	-2820.04 Hartree
RMS Gradient Norm	1.38E-06 Hartree/Bohr
Imaginary Freq	7
Dipole Moment	6.2359 Debye
Point Group	C1

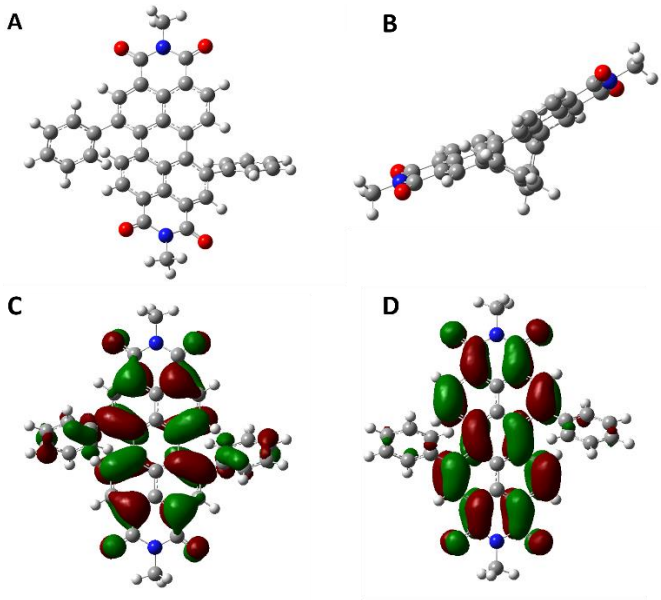


Figure S 32. 3D structures (Side view (A), top view (B)) and frontier orbitals HOMO (C), LUMO (D)) of the lowest energy conformers of **(M_2)** obtained by DFT using B3LYP/6-31G(d) basis set.

Table S 15. Symbolic Z-Matrix of **M2**, Charge=0, Multiplicity=1.

C	-4.14282	0.31679	-0.10743
C	-2.74159	0.33831	-0.10756
C	-2.05961	1.56258	-0.10755
C	-2.77887	2.76532	-0.10741
C	-4.1801	2.7438	-0.10728
C	-4.86208	1.51953	-0.10729
C	-0.65838	1.5841	-0.10768
C	-2.09689	3.98959	-0.1074
H	-5.93195	1.5031	-0.10719
C	-0.69566	4.01111	-0.10752
C	0.0236	2.80837	-0.10766
H	-0.17495	4.94587	-0.10751
C	-1.95119	-0.98338	-0.10772
C	-0.54996	-0.96186	-0.10785
C	-2.63317	-2.20765	-0.10773
C	0.13202	0.26241	-0.10783
C	0.1693	-2.1646	-0.10799
C	-1.91391	-3.41039	-0.10787
C	1.53325	0.28393	-0.10796
C	1.57053	-2.14308	-0.10812
C	-0.51268	-3.38887	-0.108
H	-2.43462	-4.34515	-0.10788
C	2.25251	-0.91881	-0.10811
H	3.32238	-0.90237	-0.10821
C	1.56342	2.83202	-0.1078
C	2.2423	4.05087	-0.10779
C	2.2794	1.63498	-0.10783
C	3.63684	4.07257	-0.10848
H	1.67755	4.99443	-0.10854
C	3.67437	1.65651	-0.10753
C	4.35315	2.87503	-0.10799
H	4.17201	5.03324	-0.10911
H	4.23862	0.71253	-0.10713
H	5.4527	2.89239	-0.10848
C	-4.17299	-2.2313	-0.10758
C	-4.85187	-3.45015	-0.10759
C	-4.88896	-1.03425	-0.10733
C	-6.24641	-3.47185	-0.10803
H	-4.28712	-4.39371	-0.10857
C	-6.28394	-1.05579	-0.10677
C	-6.96272	-2.2743	-0.10726
H	-6.78158	-4.43252	-0.10868
H	-6.84819	-0.11181	-0.10616
H	-8.06226	-2.29166	-0.10755
H	3.00471	0.85663	0.35513

H	1.03646	1.15805	-0.11841
H	-3.43875	-0.69042	0.00071
H	-5.2949	-0.0712	-0.60394
C	-2.88729	5.31128	-0.10724
O	-2.3321	6.40585	-0.10722
C	-4.9705	4.06549	-0.10712
O	-6.19748	4.0943	-0.10701
C	2.36093	-3.46477	-0.10827
O	3.58791	-3.49358	-0.10839
C	0.27772	-4.71056	-0.10816
O	-0.27747	-5.80513	-0.10818
N	1.54809	-4.68959	-0.10822
N	-4.15766	5.29032	-0.10707
C	-4.46215	6.08052	-1.30864
H	-5.50766	6.0114	-1.5255
H	-4.20011	7.10387	-1.13838
H	-3.90033	5.70149	-2.13663
C	1.85481	-5.48118	1.09186
H	1.59212	-6.50427	0.92105
H	2.90079	-5.4126	1.30665
H	1.2948	-5.10287	1.92142

Table S 16. Summary of optimization of **M_2**.

File Name	**M_2**
File Type	.log
Calculation Type	FOPT
Calculation Method	RB3LYP
Basis Set	6-31G
Charge	0
Spin	Singlet
E(RB3LYP)	-1871.35 Hartree
RMS Gradient Norm	1.02E-05 Hartree/Bohr
Imaginary Freq	36
Dipole Moment	1.4143 Debye
Point Group	C1

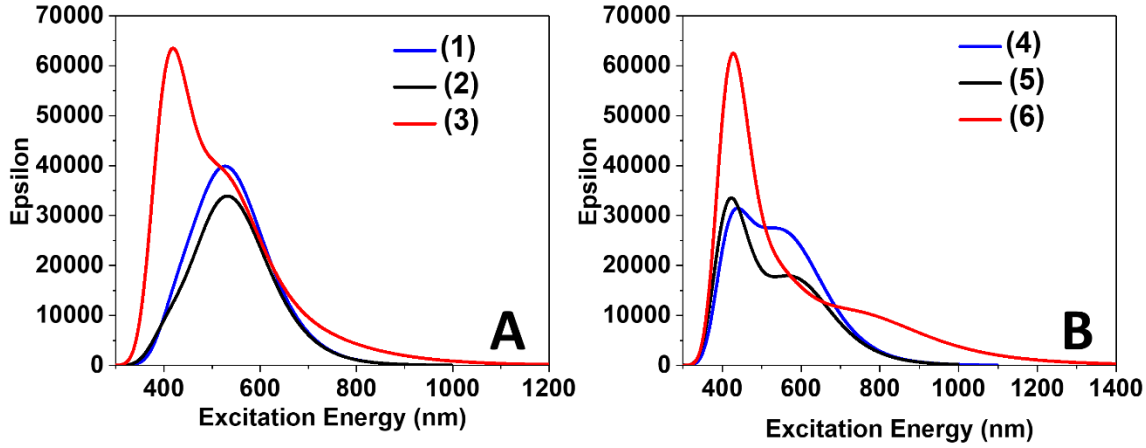


Figure S 33. TD-DFT: Estimated absorbance spectra of Azo-PBIs in gas phase.

3. Optical Properties and *E*- to *Z*- Isomerisation Studies

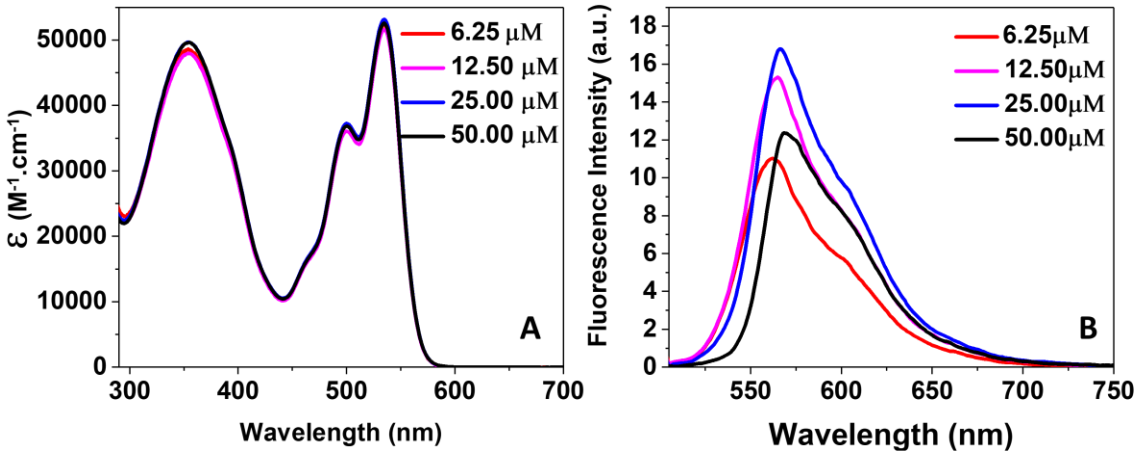


Figure S 34. Absorbance (A) and fluorescence (B) spectra of **(1)** in chloroform (λ_{ex}: 495 nm).

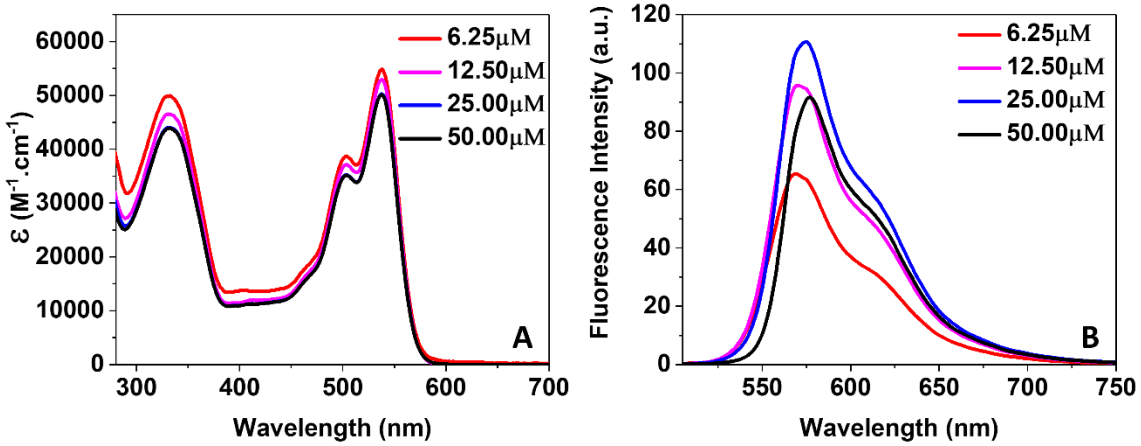


Figure S 35. Absorbance (A) and fluorescence (B) spectra of **(2)** in chloroform (λ_{ex}: 495 nm).

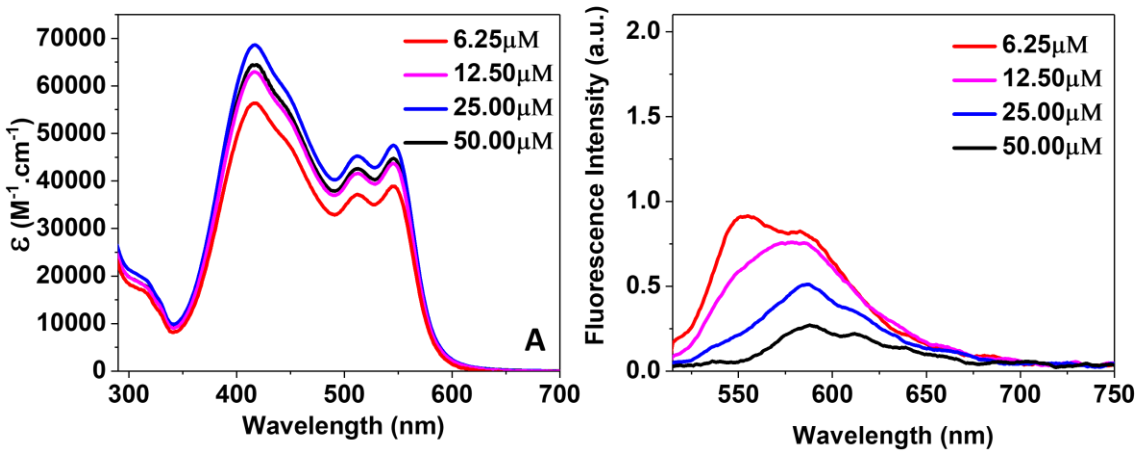


Figure S 36. Absorbance (A) and fluorescence (B) spectra of **(3)** in chloroform (λ_{ex}: 495 nm).

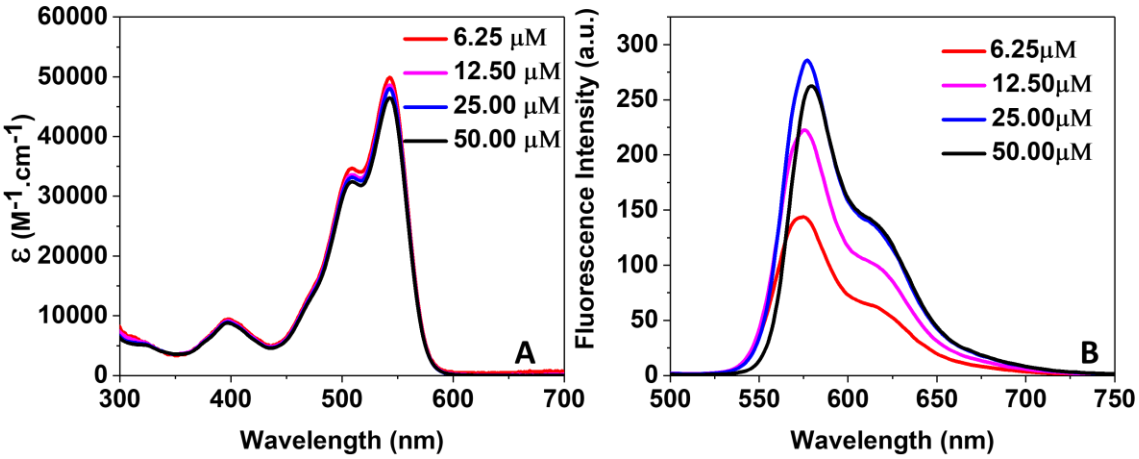


Figure S 37. Absorbance (A) and fluorescence (B) spectra of **M_1** in chloroform (λ_{ex}: 495 nm).

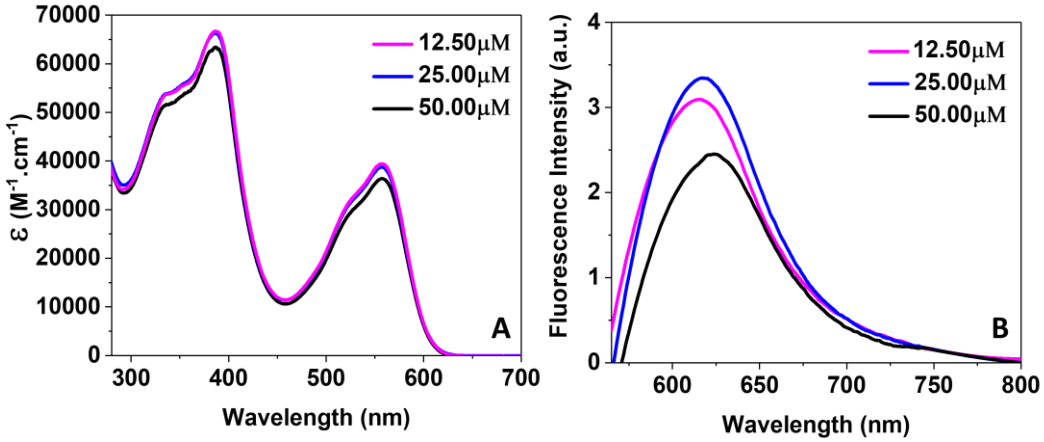


Figure S 38. Absorbance (A) and fluorescence (B) spectra of **(4)** in chloroform (λ_{ex}: 555 nm).

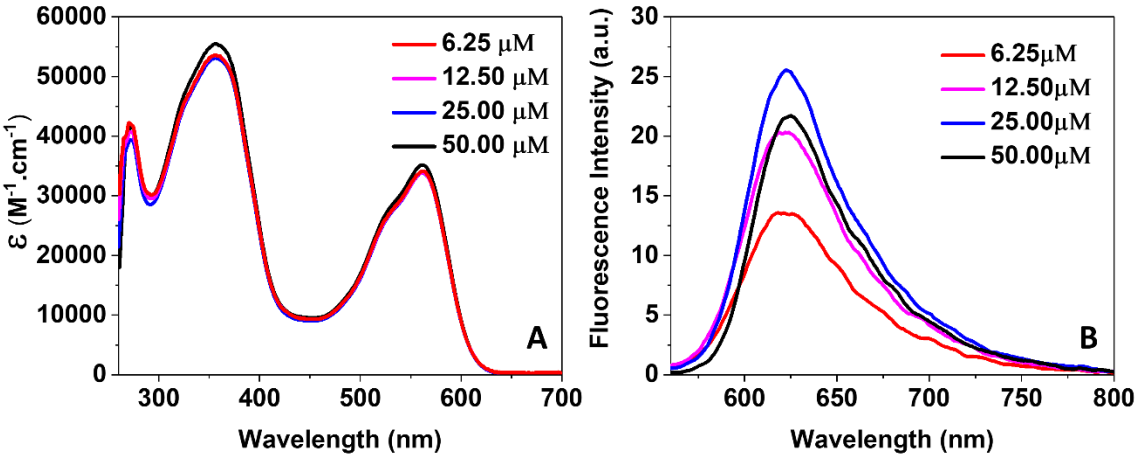


Figure S 39. Absorbance (A) and fluorescence (B) spectra of **(5)** in chloroform (λ_{ex}: 555 nm).

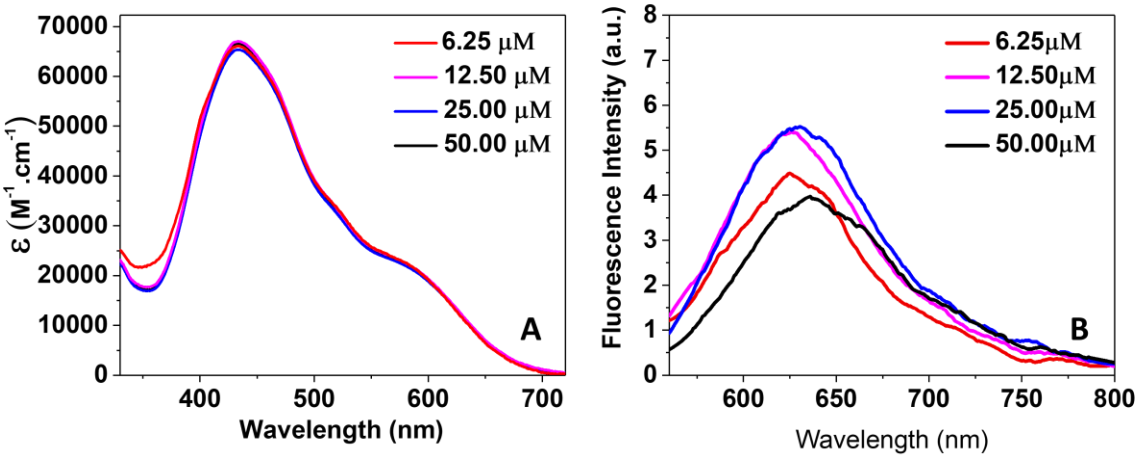


Figure S 40. Absorbance (A) and fluorescence (B) spectra of **(6)** in chloroform (λ_{ex}: 550nm).

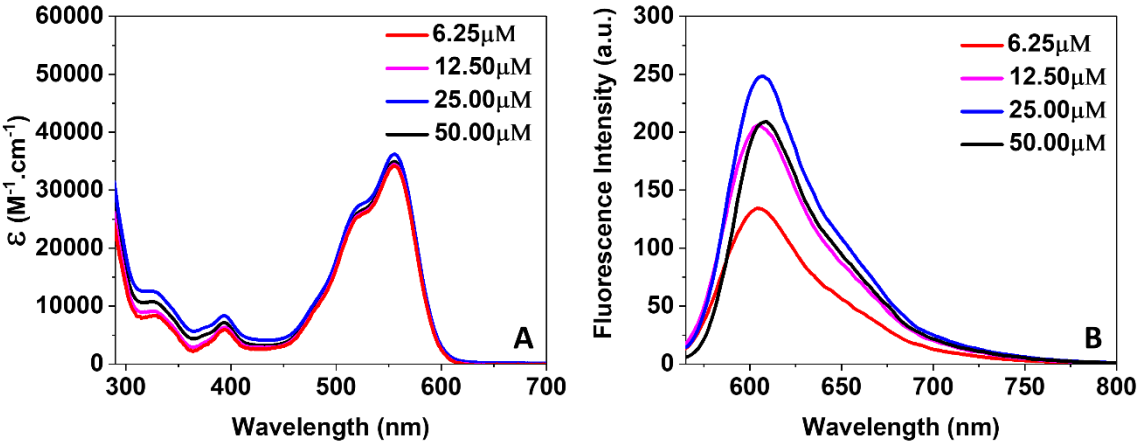


Figure S 41. Absorbance (A) and fluorescence (B) spectra of $\mathbf{M_2}$ in chloroform (λ_{ex}: 555 nm).

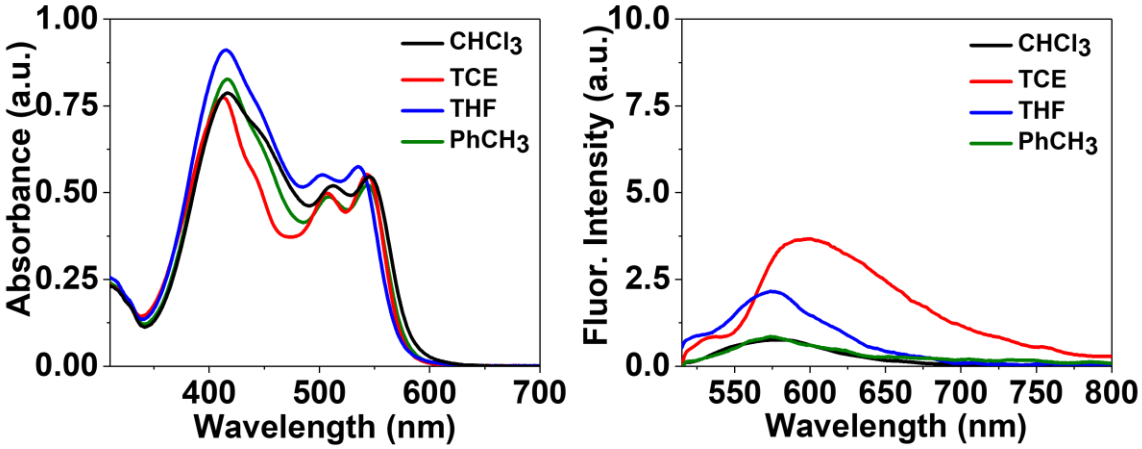


Figure S 42. Optical properties of **(3)** in different solvents: absorbance (A), emission (B) spectra (concentration - 12.50μM; excitation wavelength λ_{ex}= 495 nm).

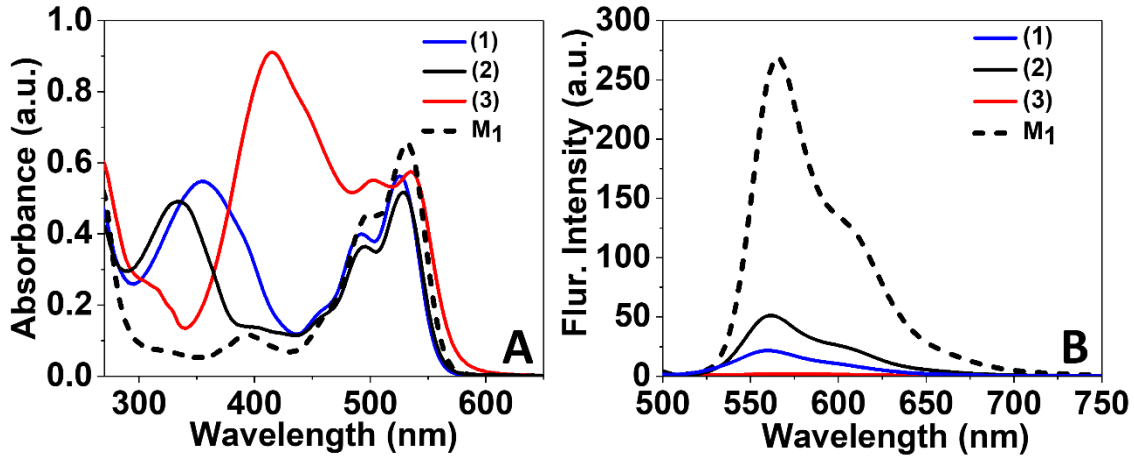


Figure S 43. Absorbance (A) and emission (B) spectra of **(1)**, **(2)**, **(3)** and **M_1** in THF (concentration - 12.50μM; excitation wavelength λ_{ex}= 495 nm).

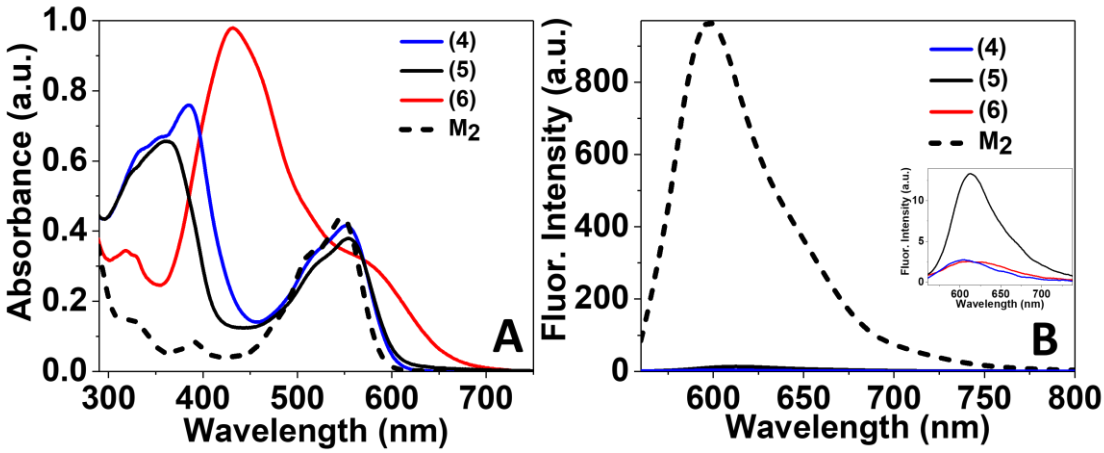


Figure S 44. Absorbance (A) and emission (B) spectra of **(4)**, **(5)**, **(6)** and **M_2** in THF (12.50μM; λ_{ex}=550 nm; inset: zoom-in on the fluorescence spectra of **4** - **6**).

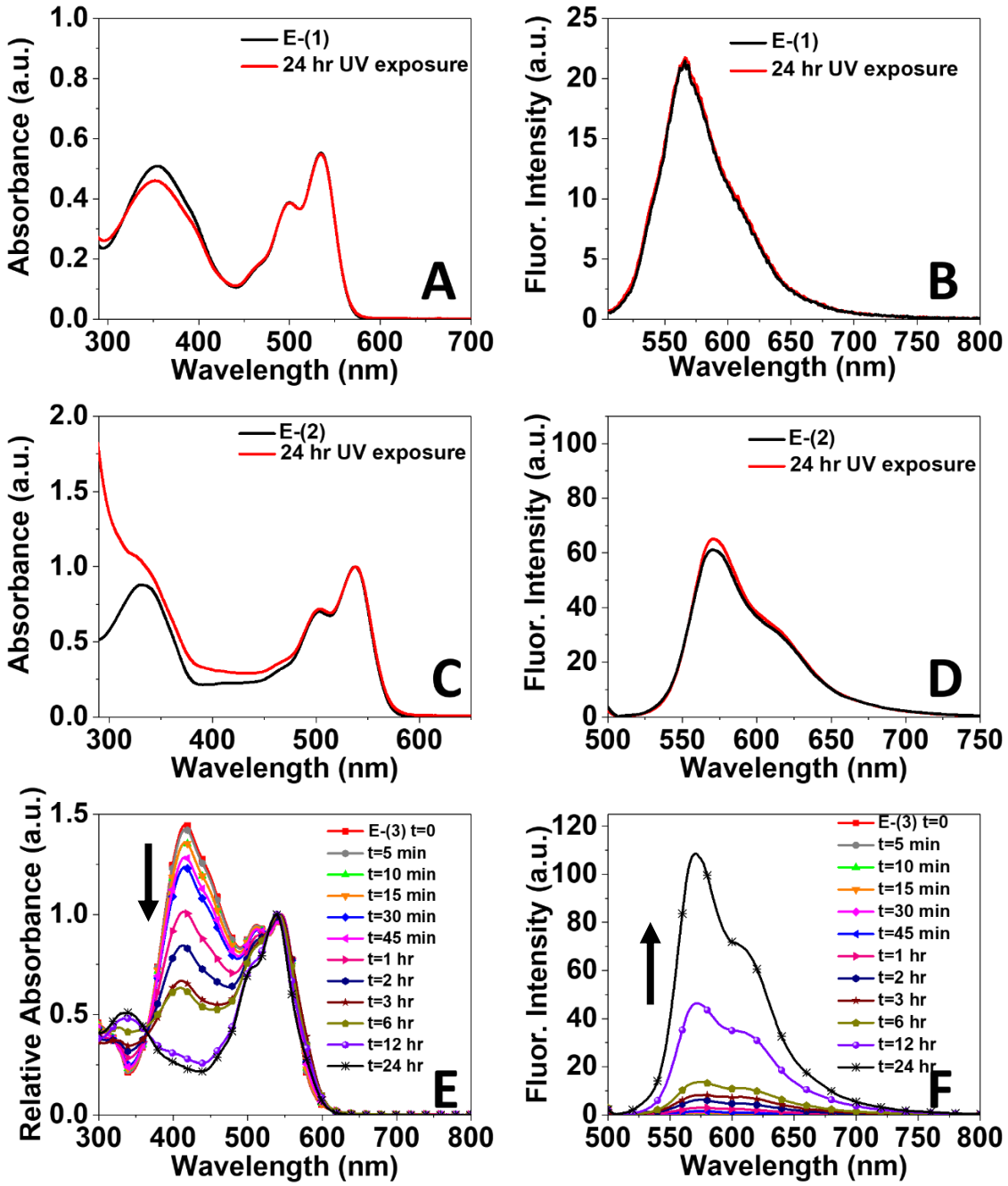


Figure S 45. The effect of *E*- to *Z*- isomerisation of azo-PBIs on optical properties in chloroform (λ_{ex}=495 nm): **(1)** (A, B), **(2)** (C, D), **(3)** (E,F).

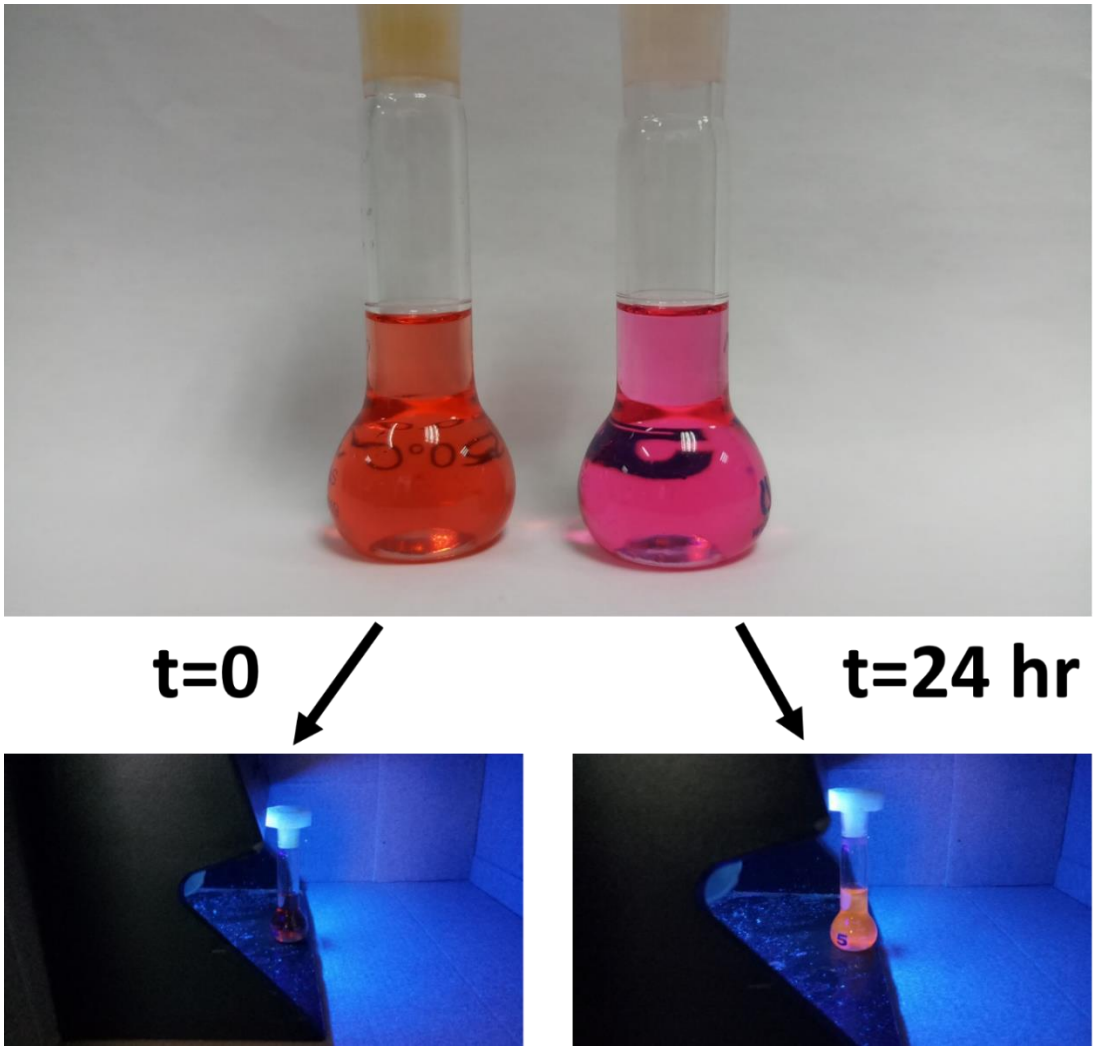


Figure S 46. Color change of **3** upon *E*- to *Z*- isomerisation.

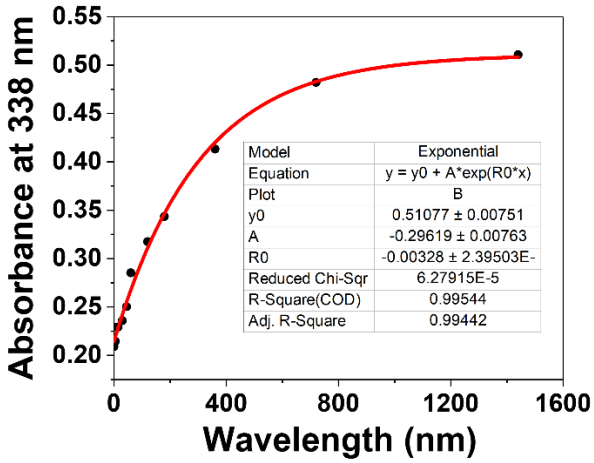


Figure S 47. Exponential fitting of *E*- to *Z*- transformation using absorbance values at 338 nm (Refer: Figure S45-E): (Complete conversion takes around 1/R0 ≈ 305 min).

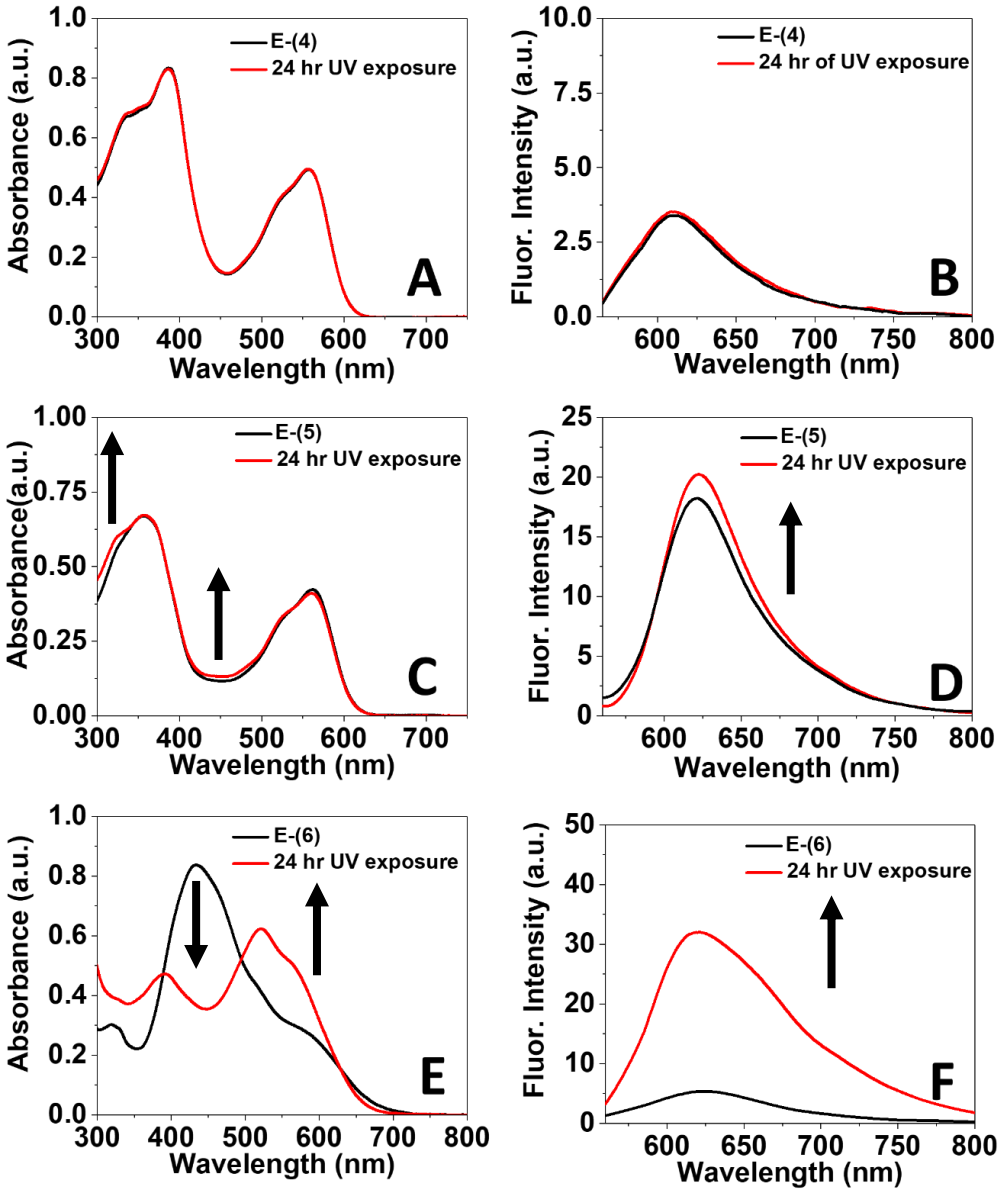


Figure S 48. The effect of *E*- to *Z*- isomerisation of azo-PBIs on optical properties in chloroform (λ_{ex}=550 nm): **(4)** (A, B), **(5)** (C, D), **(6)** (E,F).

Table S17. *E*-/*Z*- ratios of azo compounds upon 24 hours of 352 nm UV light exposure.

Compounds	***E*- %**	***Z*- %**
1	90.6	9.4
2	18.8	81.2
3	16.3	83.7
4	99.5	0.5
5	88.7	11.3
6	44.0	56.0

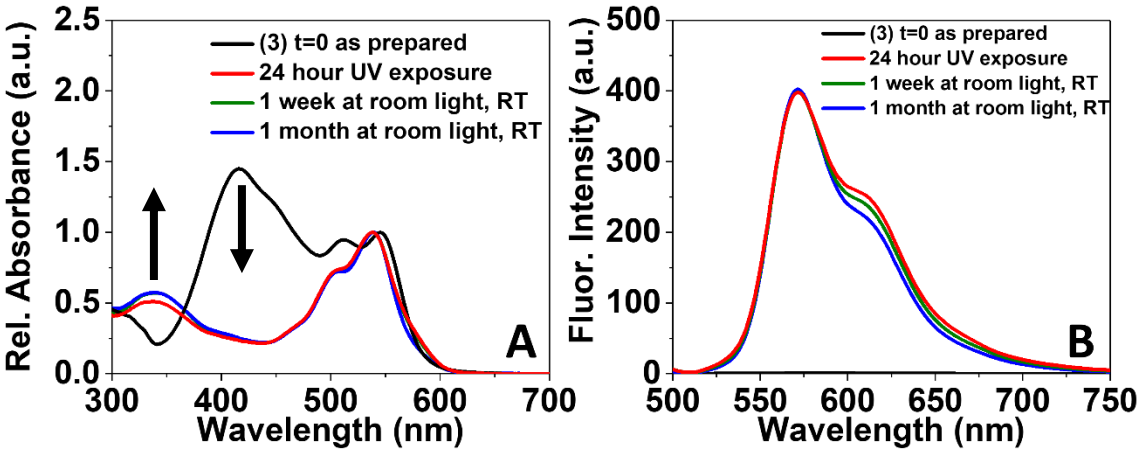


Figure S 49. Stability test of **(3)** over 1 month in chloroform (λ_{ex}=495 nm).

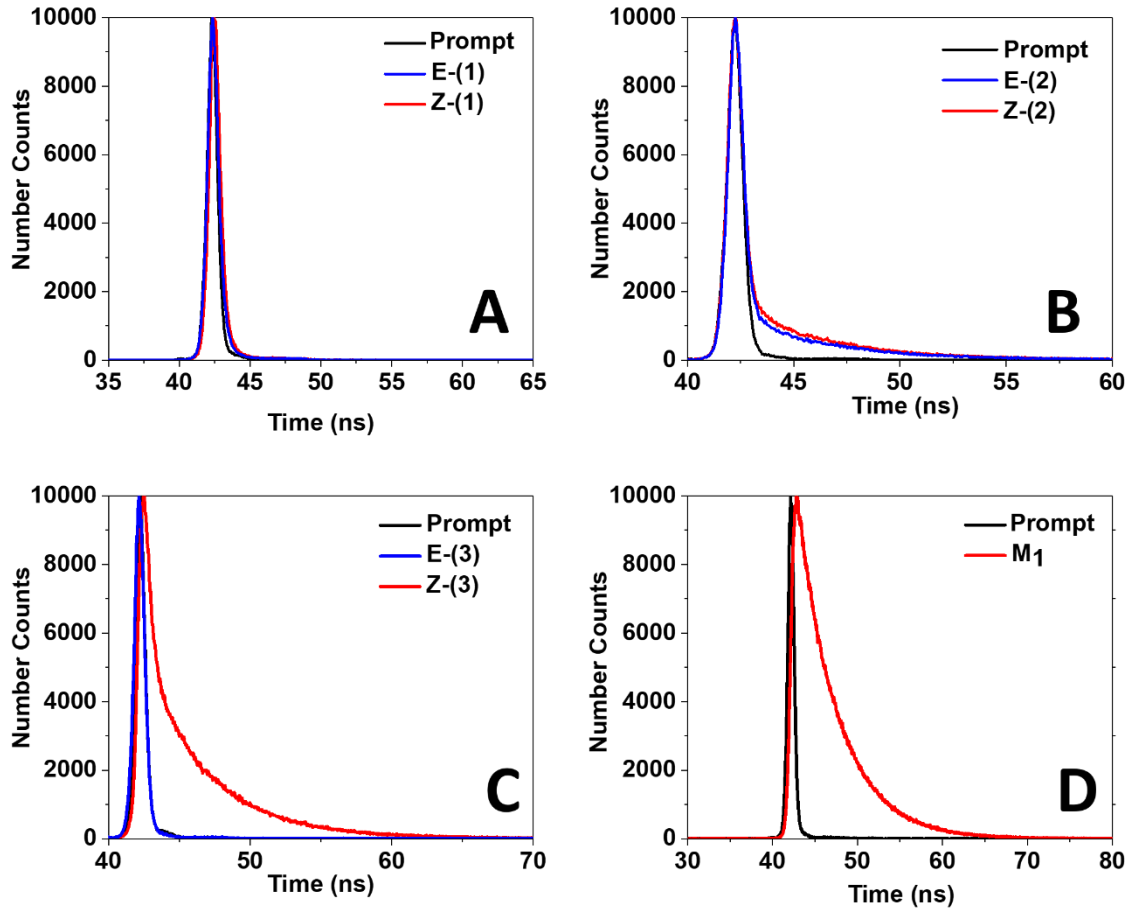


Figure S 50. Time-correlated single photon counting (TCSPC) lifetime graphs of **(1)** (A), **(2)** (B), **(3)** (C) and **M_1** (D) before and after 24 hr of 352 nm light exposure.

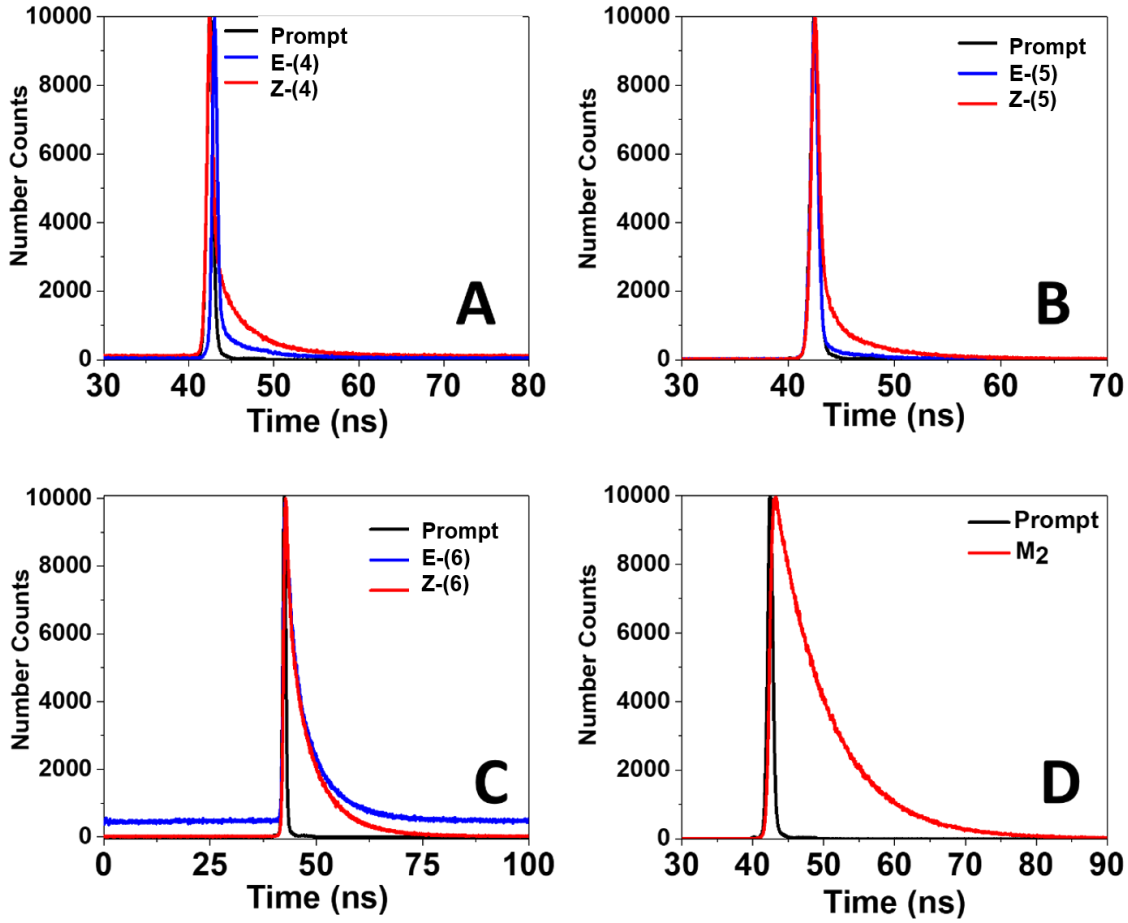


Figure S 51. Time-correlated single photon counting (TCSPC) lifetime graphs of **(4)** (A), **(5)** (B), **(6)** (C) and **M**$_2$ (D) before and after 24 hr of 352 nm light exposure.

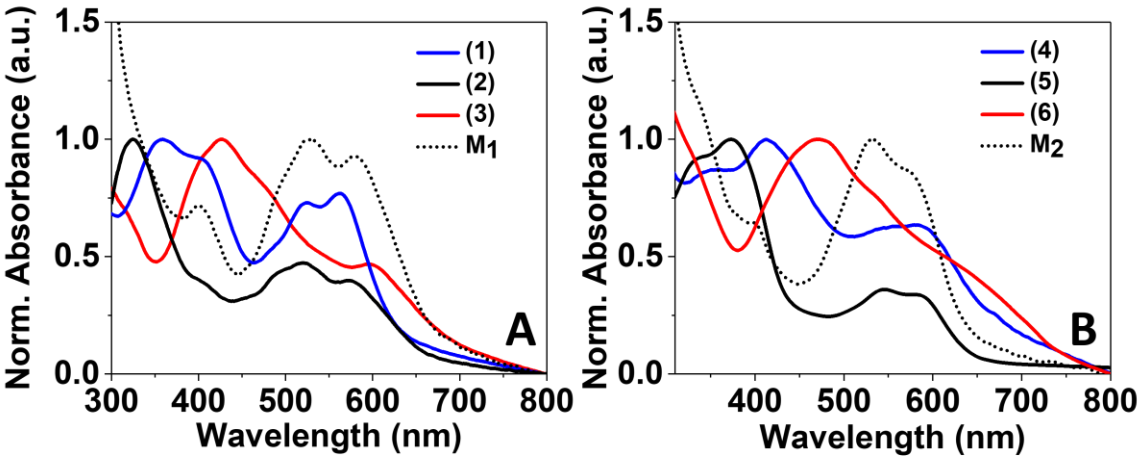


Figure S 52. Normalized absorbance spectra of **(1)**, **(2)**, **(3)**, **M**$_1$ (A), **(4)**, **(5)**, **(6)** and **M**$_2$ (B) in solid state.

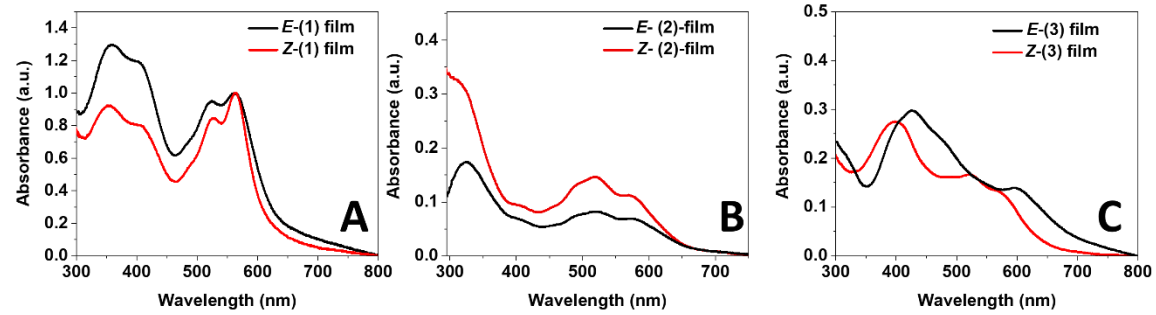


Figure S 53. Solid state UV-Vis spectra of *E*- and *Z*- **(1)** (A), *E*- and *Z*- **(2)** (B), *E*- and *Z*- **(3)** (C).

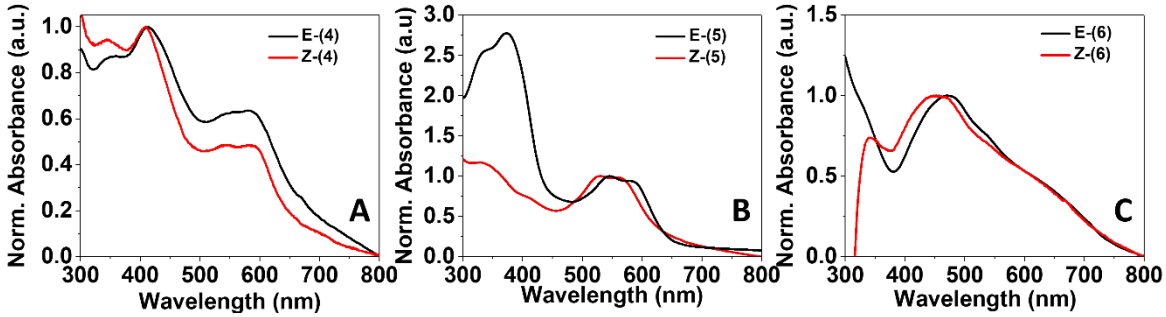


Figure S 54. Solid state UV-Vis spectra of *E*- and *Z*- **(4)** (A), *E*- and *Z*- **(5)** (B), *E*- and Z- **(6)** (C).

4. Electrochemistry (CV)

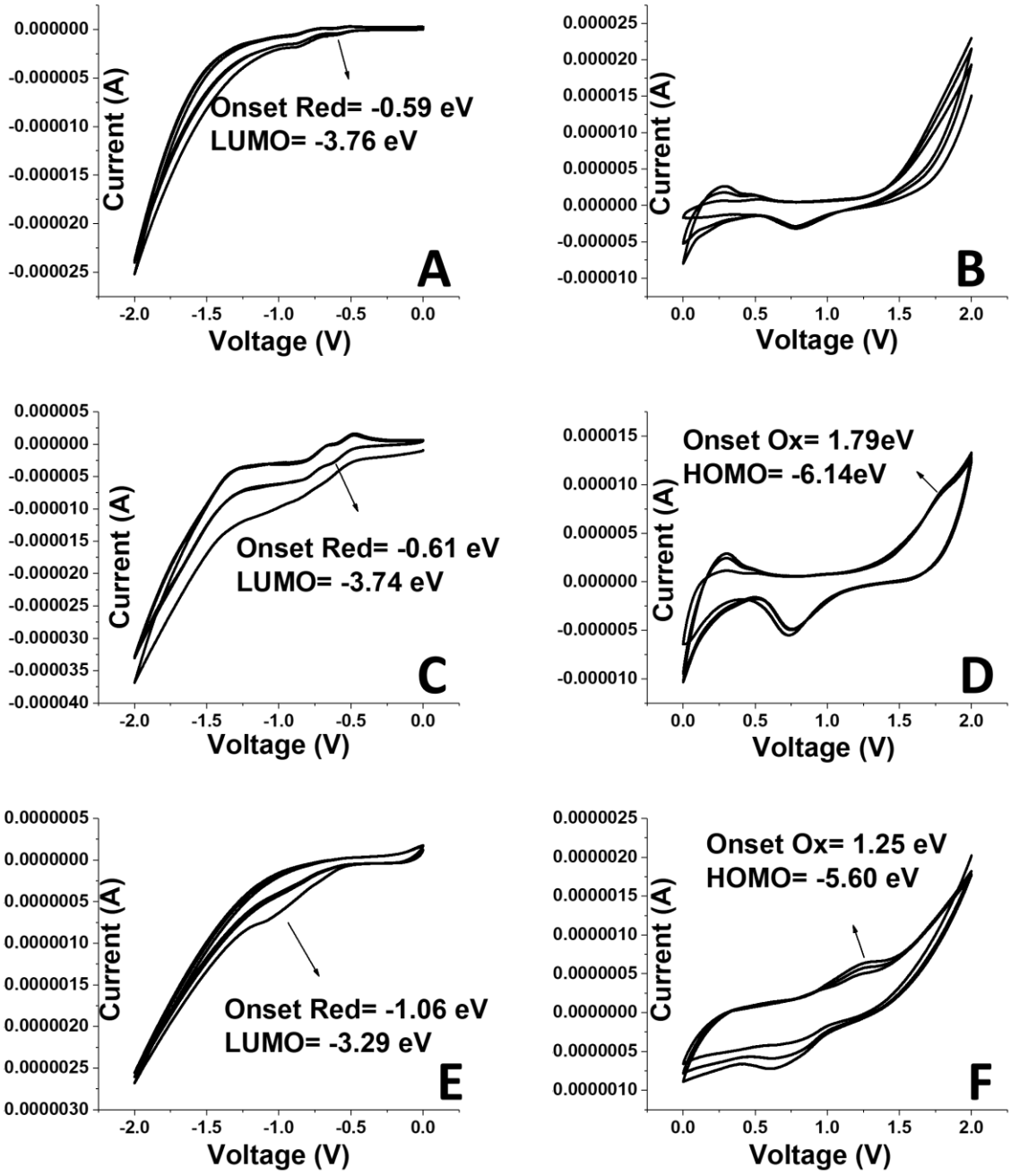


Figure S 55. Oxidation (A, C, E) and reduction (B, D, F) curves of non-conjugated Azo-PBI derivatives: **(1)** (A, B), **(2)** (C, D), **(3)** (E, F).

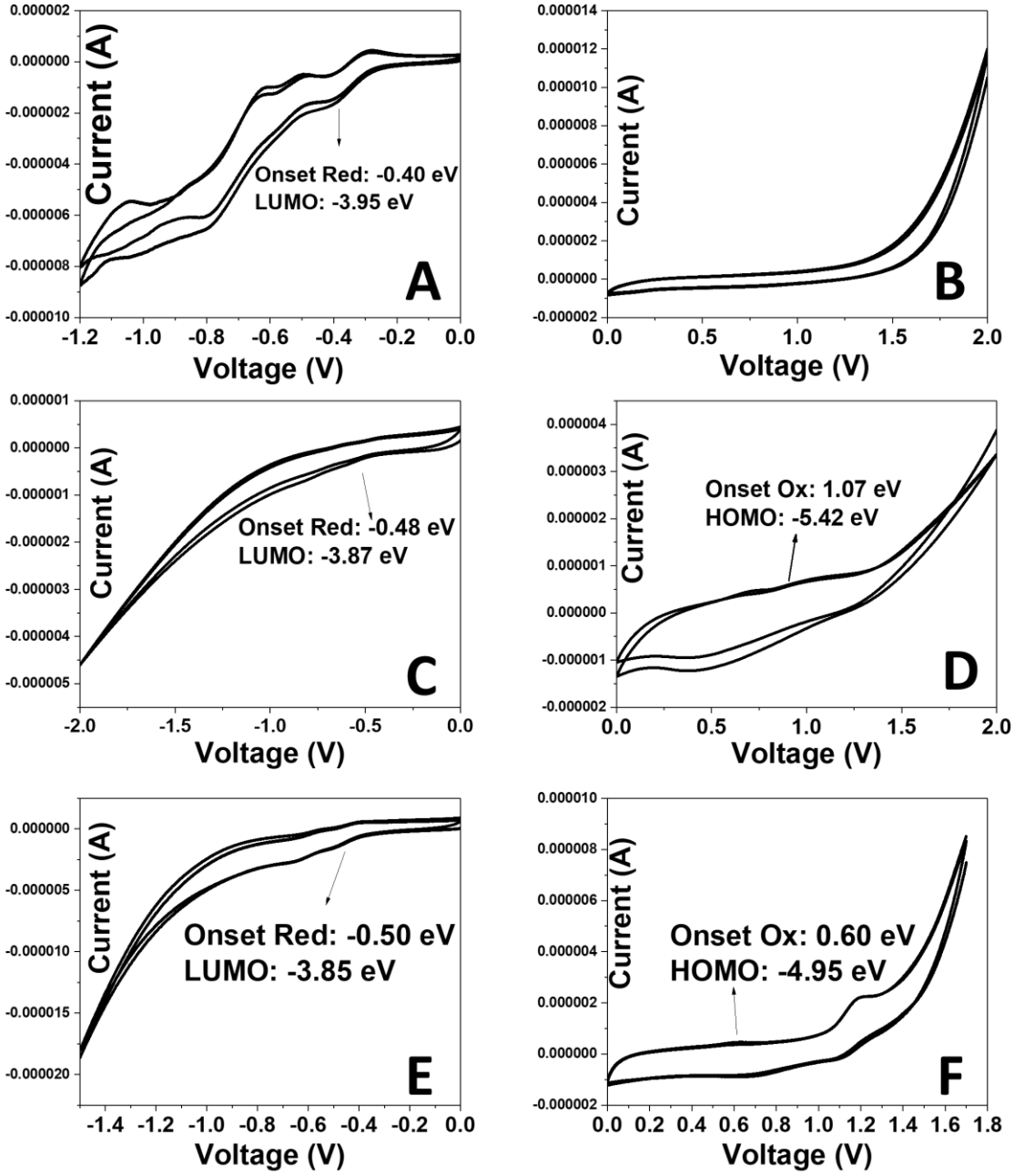


Figure S 56. Oxidation (A, C, E) and reduction (B, D, F) curves of conjugated Azo-PBI derivatives: **(4)** (A, B), **(5)** (C, D), **(6)** (E, F).

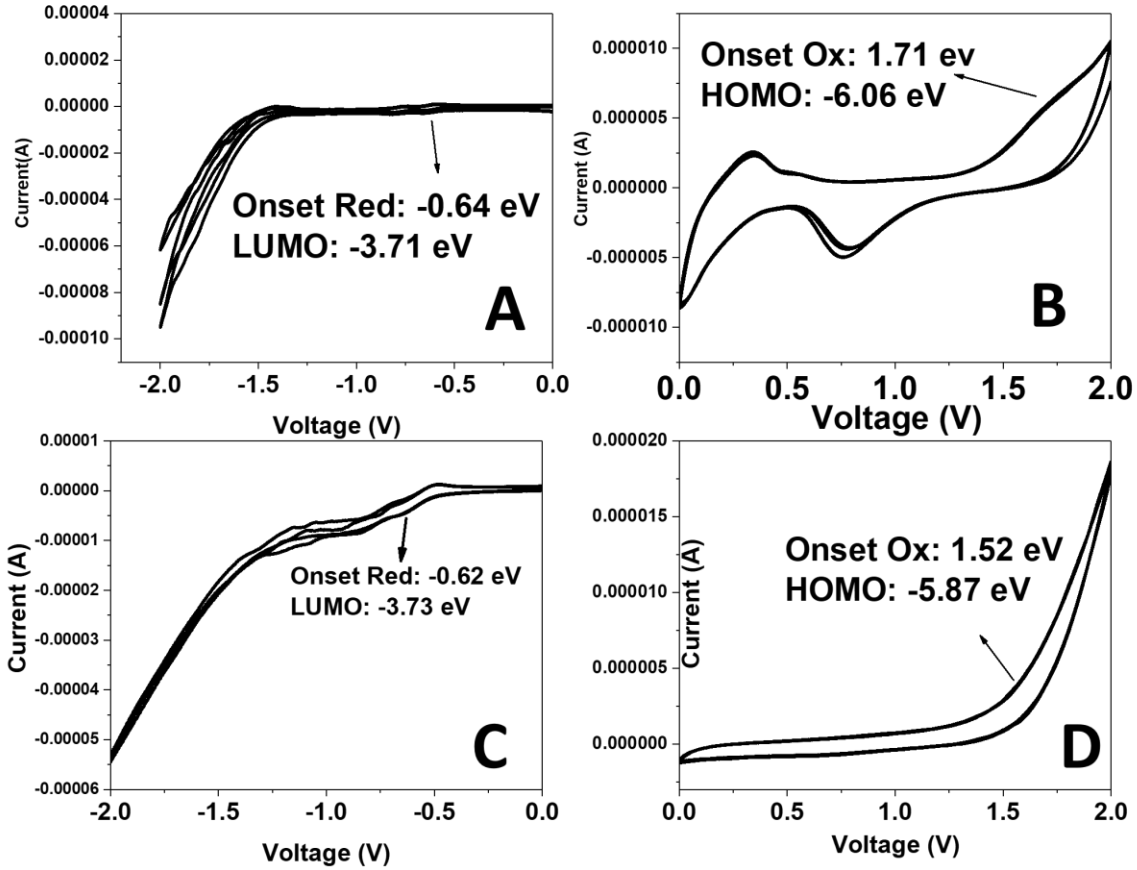


Figure S 57. Oxidation (A, C) and reduction (B, D) curves of model PBIs: **(M_1)** (A, B), **(M_2)** (C, D).

5. Thermogravimetry (TGA)

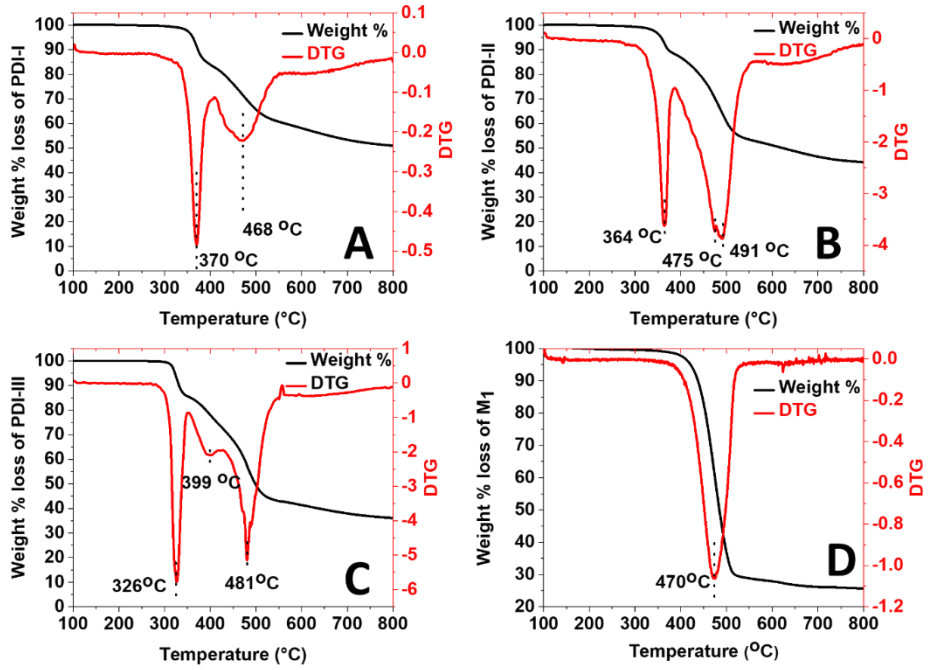


Figure S 58. TG/DTG of non-conjugated azo-PBIs compared to model M_1: **(1)**(A), **(2)** (B), **(3)** (C), **M_1** (D).

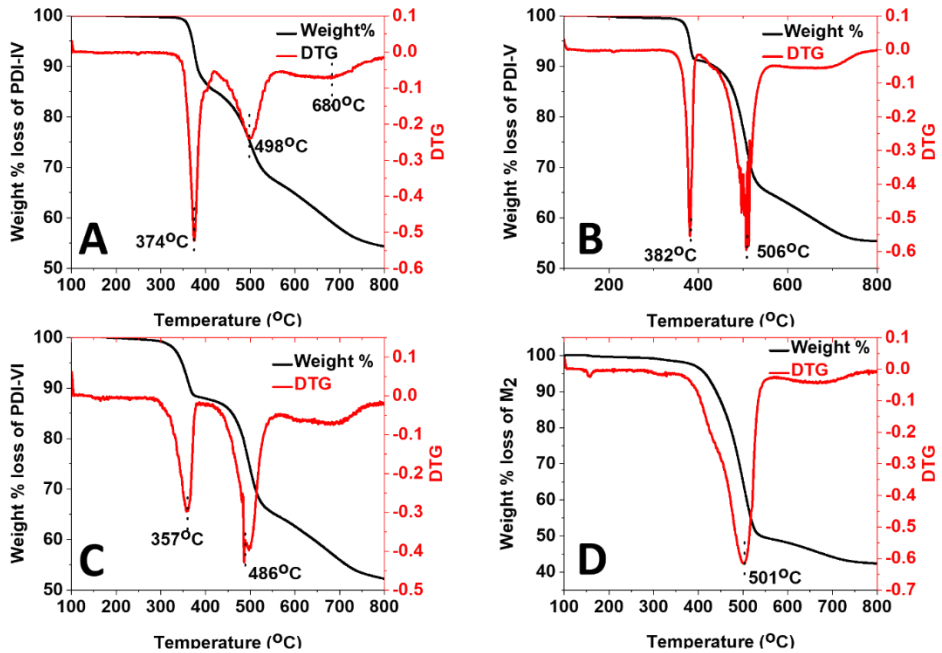


Figure S 59. TG/DTG of conjugated azo-PBIs compared to model M_2: **(4)**(A), **(5)** (B), **(6)** (C), **M_2** (D).

6. Self-Assembly Studies and Optical Titrations

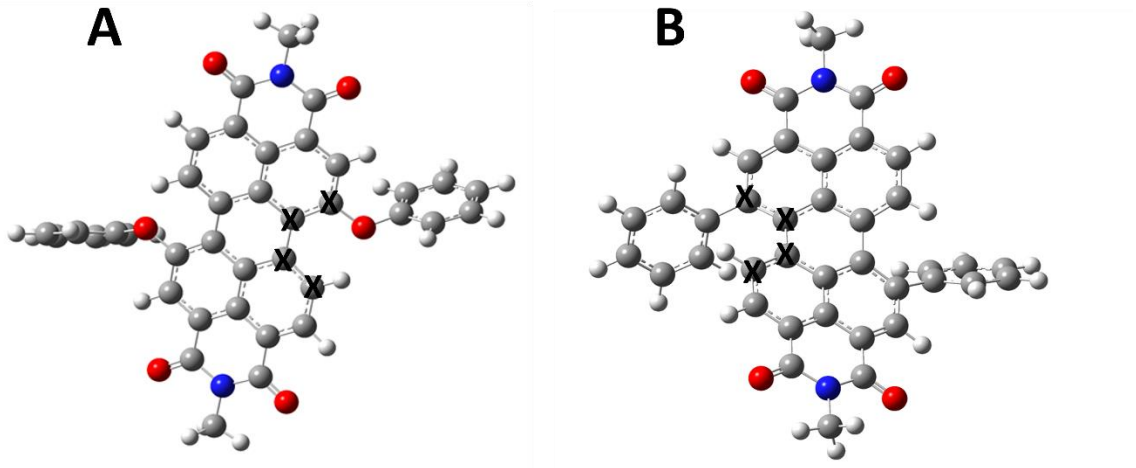


Figure S 60. The defined dihedral angle (Chosen atoms were denoted as X): A is representative of nonconjugated azo-PBIs, B is representative of conjugated azo-PBIs.

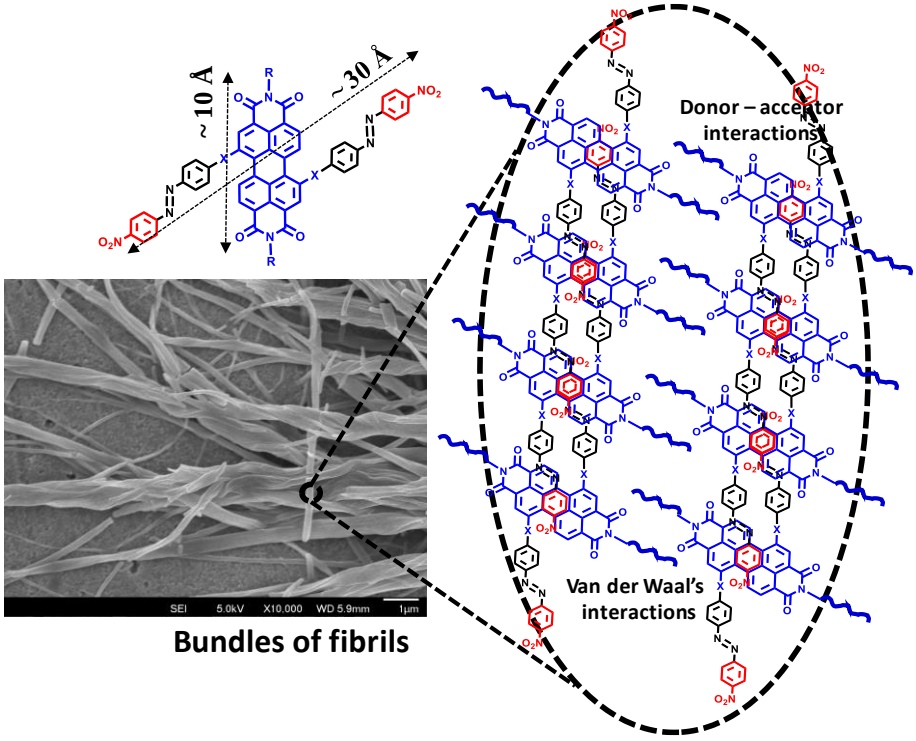


Figure S 61. A tentative self-assembly model for azo-PBIs, using compound **1** as a model structure.

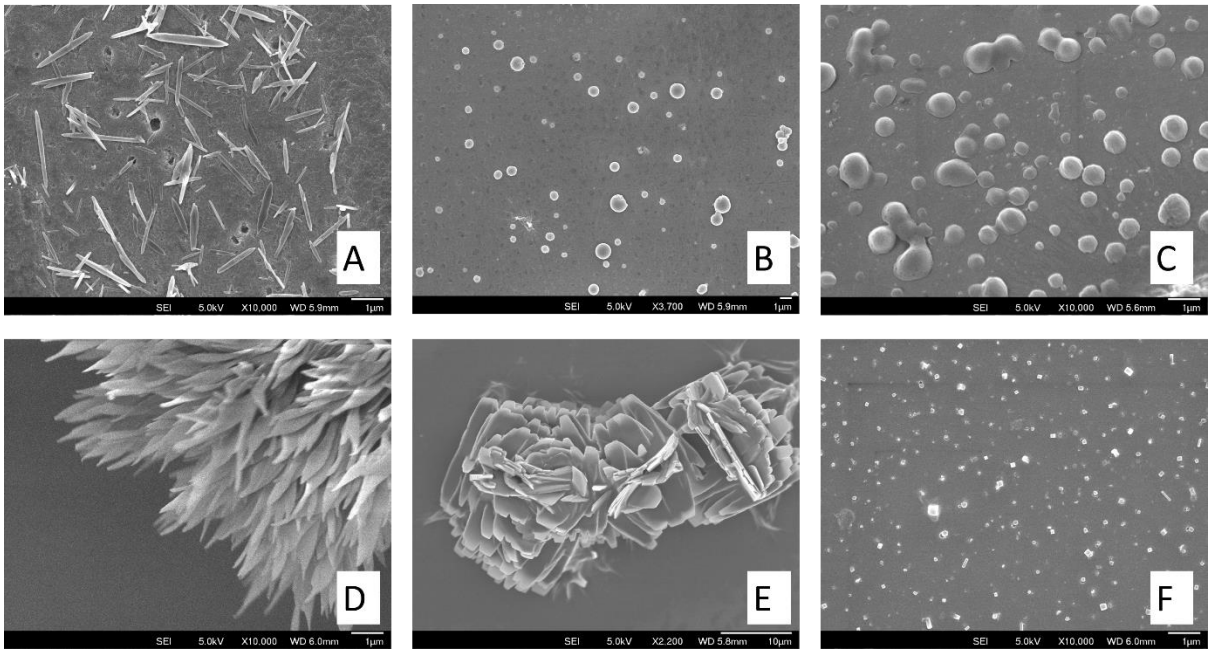


Figure S 62. Self-Assembly of **(1)** (A), **(2)** (B), **(3)** (C), **(4)** (D), **(5)** (E), **(6)** (F) upon 1 week of 352 nm UV light exposure obtained by FESEM through several magnifications.

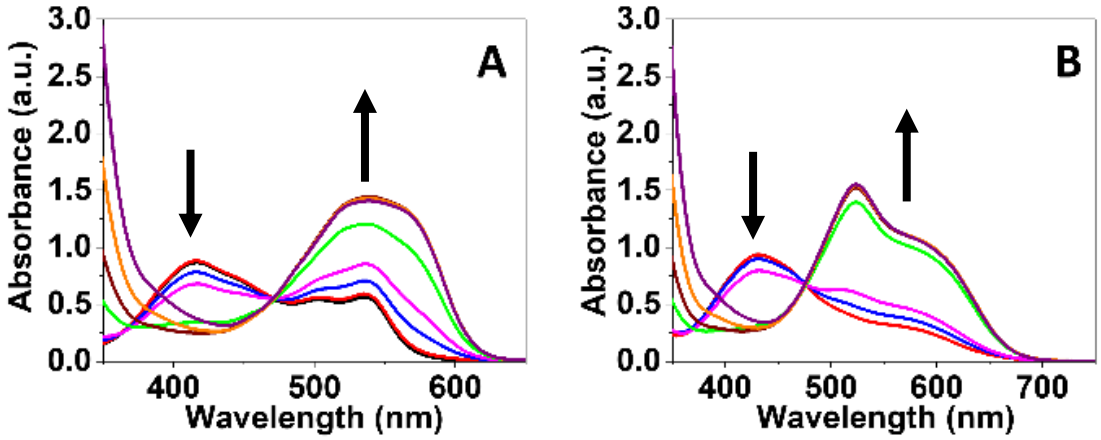


Figure S 63. Titrimetric absorbance spectra of 12.50 µM of **(3)** (A) and 12.50 µM **(6)** (B) with different amounts of $HAuCl_4$. (0 eq –), (0.5 eq –), (1 .0 eq–), (2.0 eq–), (10.0 eq –), (20.0 eq –), (40.0 eq –), (70.0 eq –).

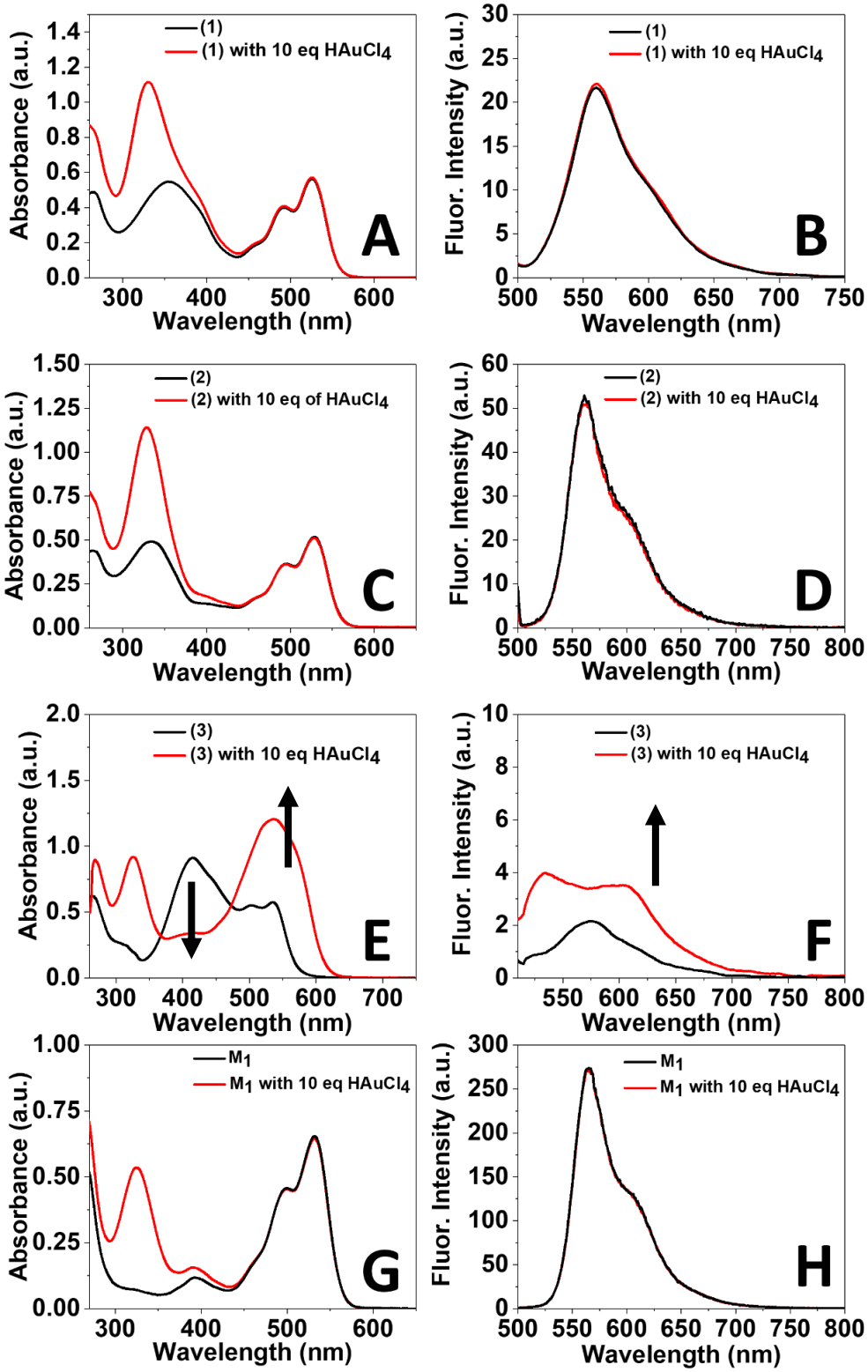


Figure S 64. Titrimetric absorbance (A, C, E, G) and fluorescence (B, D, F, H) spectra of **(1)** (A, B), **(2)** (C,D), **(3)** (E, F) and **M1** (G, H) with $HAuCl_4$ in THF.

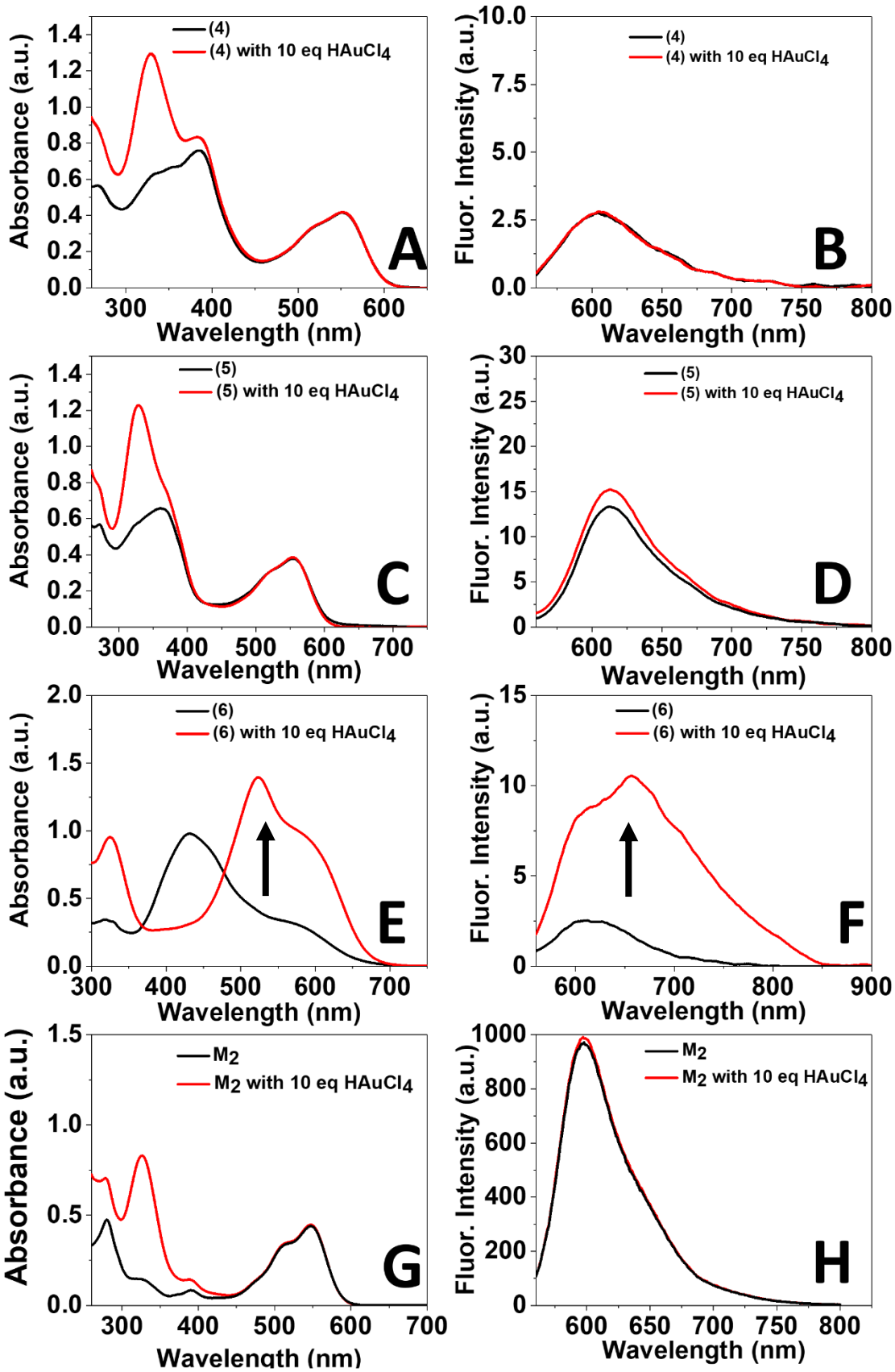


Figure S 65. Titrimetric absorbance (A, C, E, G) and fluorescence (B, D, F, H) spectra of **(4)** (A, B), **(5)** (C,D), **(6)** (E, F) and **M**$_2$ (G, H) with $HAuCl_4$ in THF.

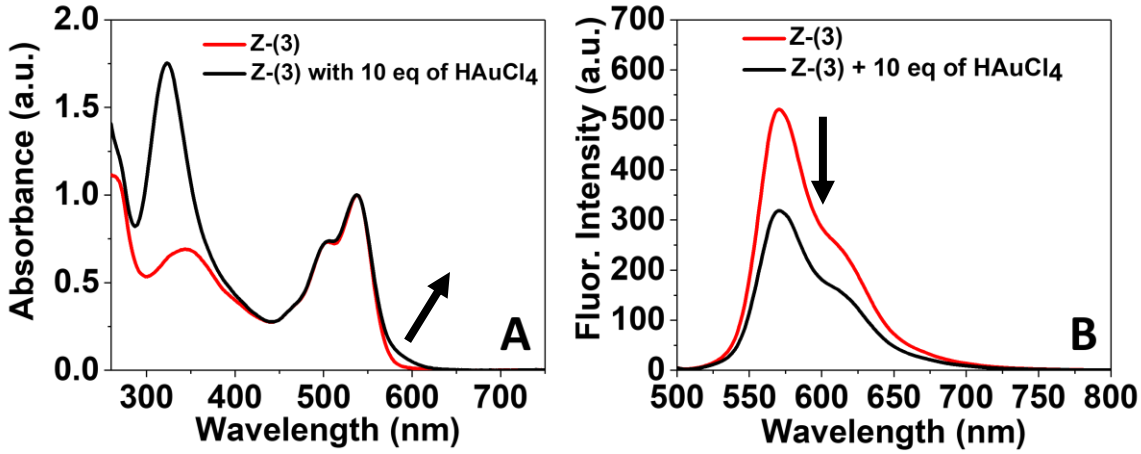


Figure S 66. Titration of 12.50μM *Z*-**(3)** with 10 eq of $HAuCl_4$ in THF : $CHCl_3$ (12.5:87.5).

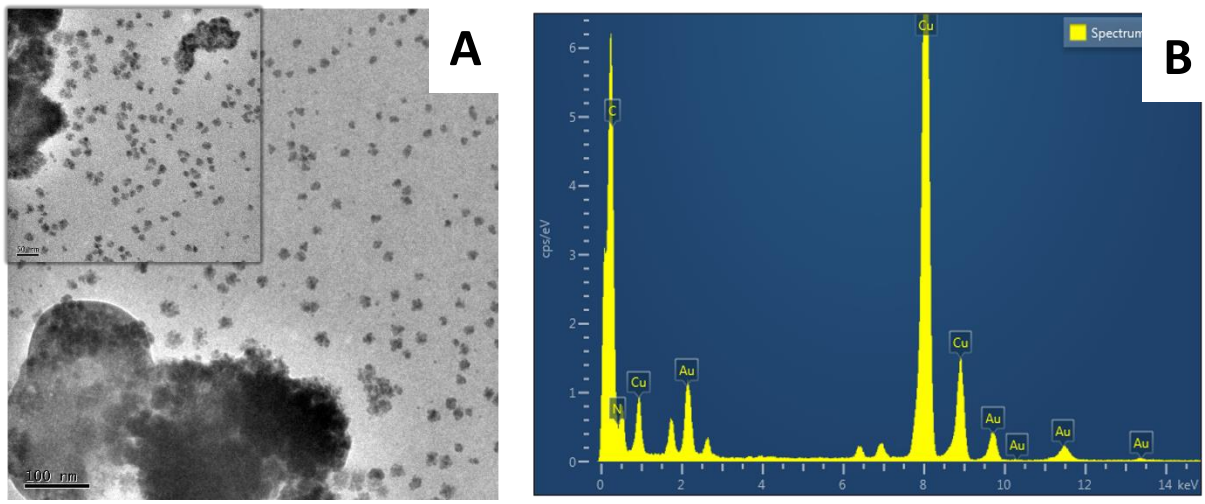


Figure S 67. TEM (A) and EDS (B) analysis of thin films of reduced gold particles from compound **3**.

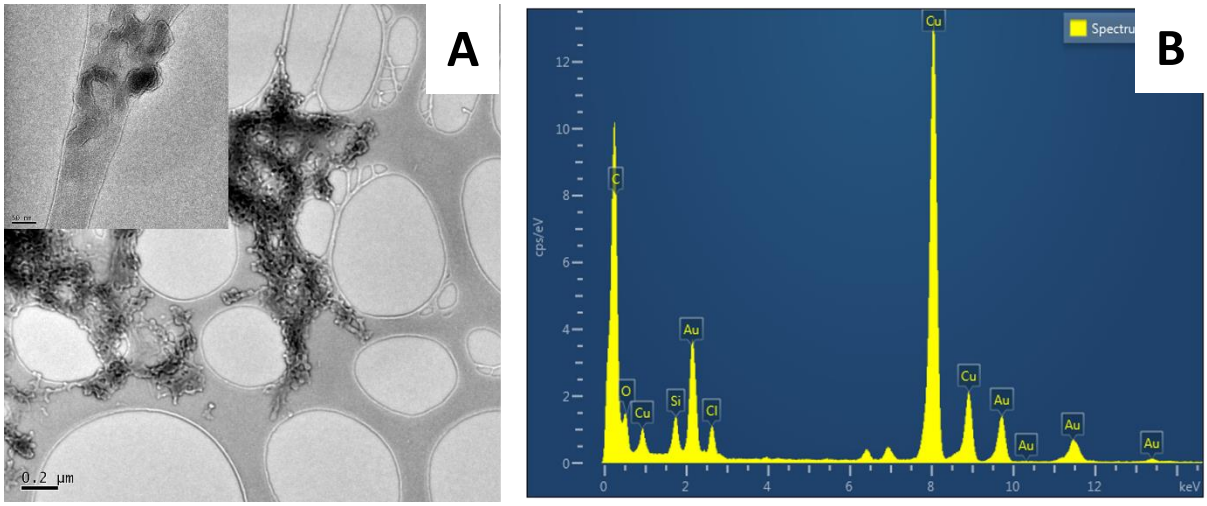


Figure S 68. TEM (A) and EDS (B) analysis of the thin film of reduced gold particles from compound **6**.

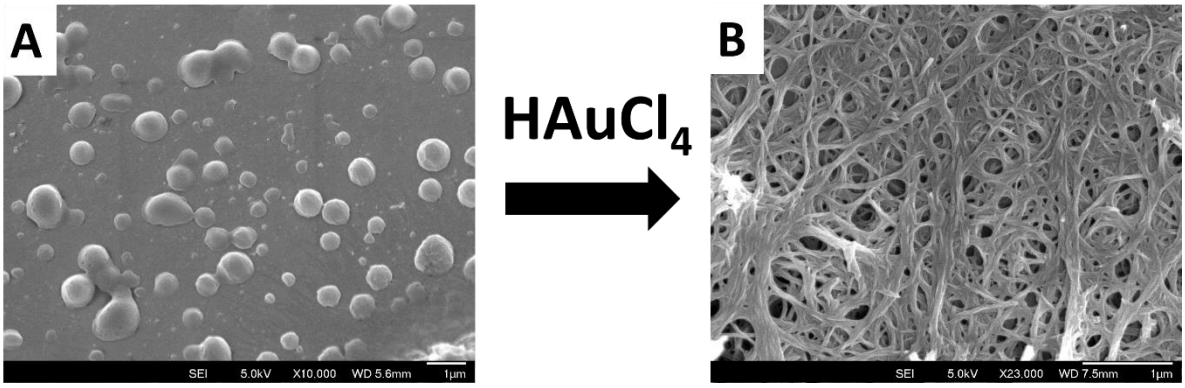


Figure S 69. Self-Assembly of *Z*-**(3)** without (A) and with (B) $HAuCl_4$.