Bis-Naphthalimides Bridged by Electron Acceptors: Optical and Self-assembly Characteristics

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Electronic Supplementary Information

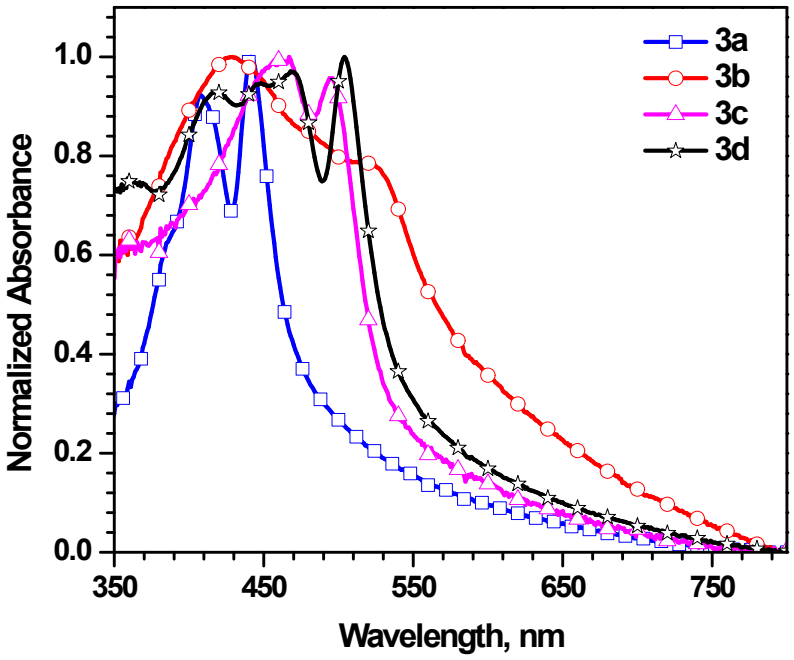

Fig. S1 Normalized absorption spectra of dyes as dropcasted thin films.

Sample preparation for THF: H_2O titration studies

Prepared stock solution of dyes in THF (2×10^{-4} M) and diluted ten times to 2×10^{-5} M. Sample solutions (10 mL) with varying water concentration (distilled water) from 0% to 90% in THF solution with same concentration is prepared for absorption. The same solution system is diluted 10 times with THF and water keeping constant concentration of 2×10^{-6} M for emission.

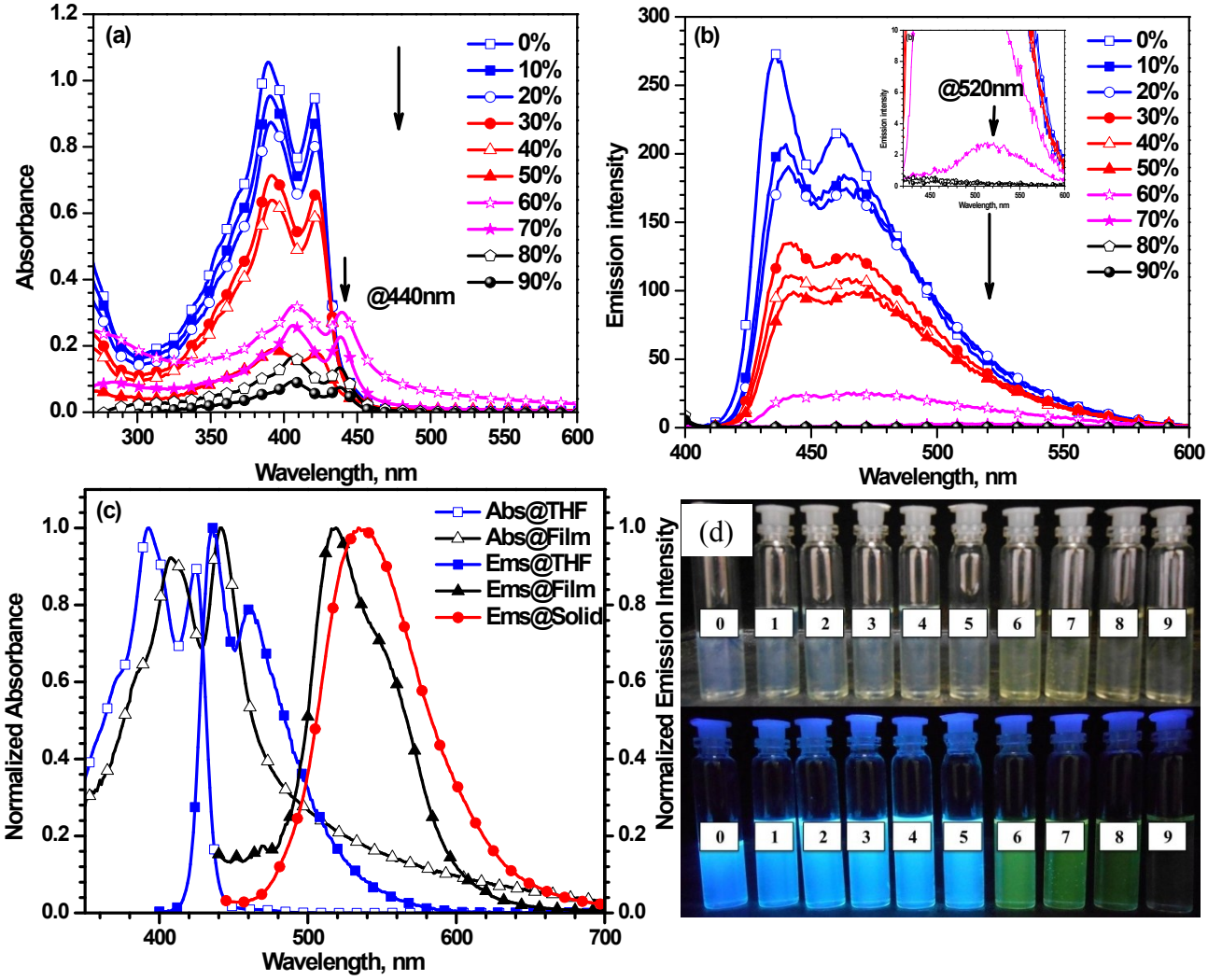

Fig. S2. (a, b) Absorption and emission spectra of **3a** with THF:H_2O titration studies respectively. (**c**) Normalized absorption and emission spectra of THF solution, thin film and solid state (**d**) Images of solution (above under normal light, below under UV light) obtained by varying water concentration in THF solvent for **3a** (left to right – increasing water concentration 0-90%)

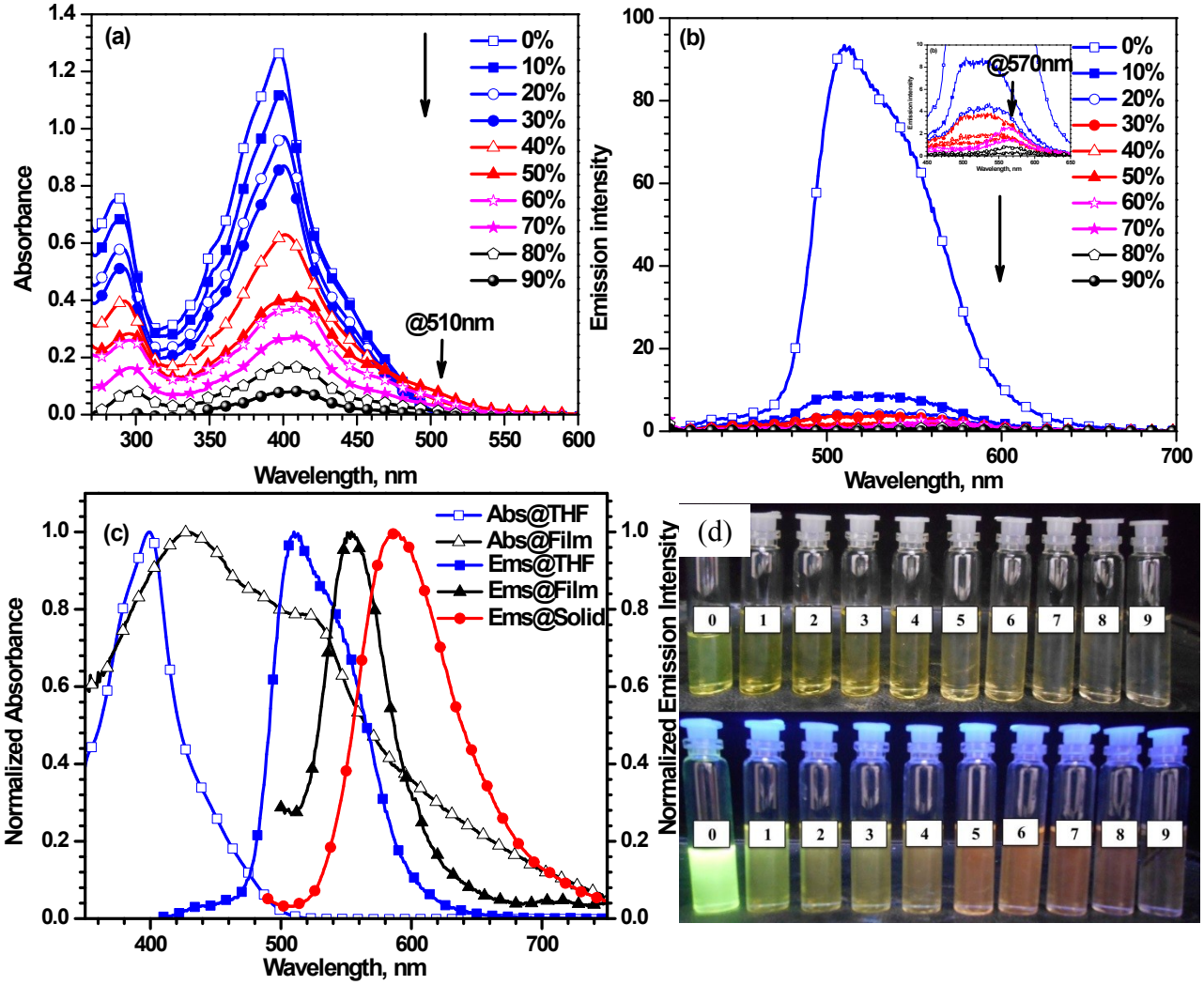

Fig. S3. (a, b) Absorption and emission spectra of **3b** with THF:H_2O titration studies respectively. (**c**) Normalized absorption and emission spectra of THF solution, thin film and solid state (**d**) Images of solution (above under normal light, below under UV light) obtained by varying water concentration in THF solvent for **3b** (left to right – increasing water concentration 0-90%)

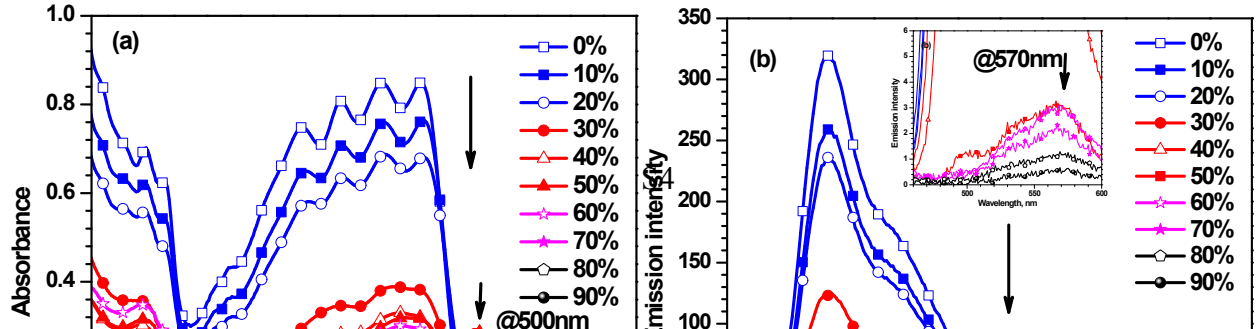

Fig. S4 (a, b) Absorption and emission spectra of **3d** with THF:H_2O titration studies respectively. (**c**) Normalized absorption and emission spectra of THF solution, thin film and solid state (**d**) Images of solution (above under normal light, below under UV light) obtained by varying water concentration in THF solvent for **3d** (left to right – increasing water concentration 0-90%)

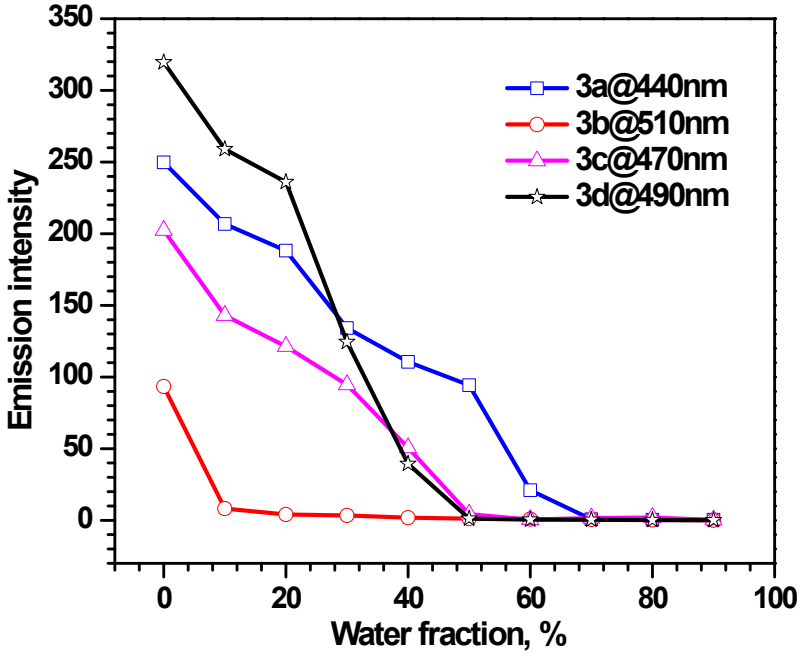

Fig. S5 Plot of emission intensity vs water fraction in THF solvent for dyes.

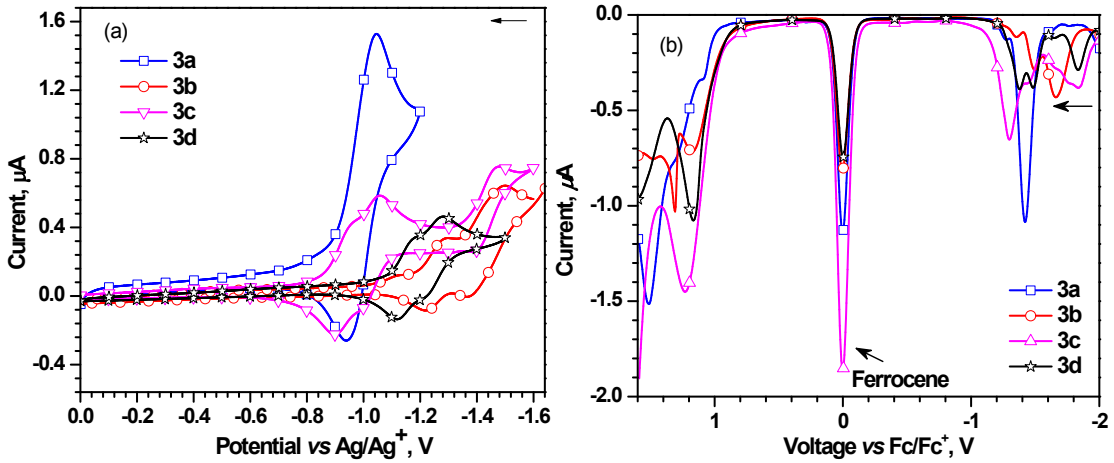

Fig. S6 (a) Cyclic voltammetry (CV) of the dyes showing reduction region (b) Differential pulse voltammetry (DPV)

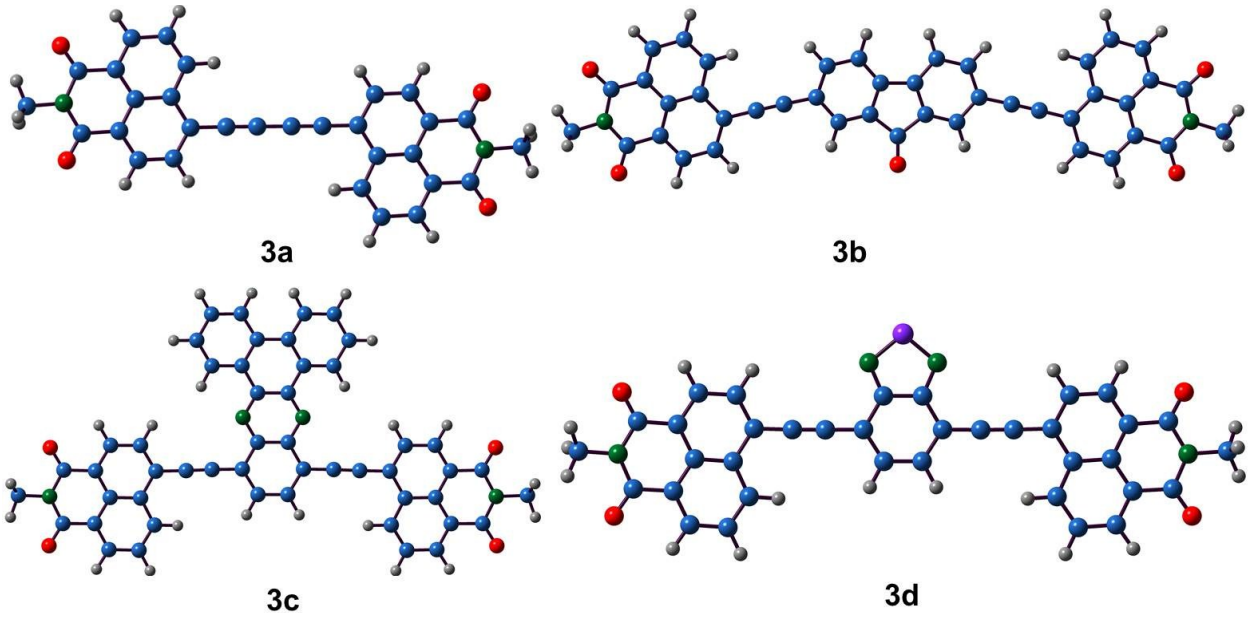

Fig. S7 Optimized geometries for **3a, 3b, 3c**, and **3d** by DFT calculations using B3-LYP 6-31G(d, p) functionals

Sample preparation for SEM morphological studies

As synthesized samples: On the aluminium holder sample is spread and sputtered with gold particles under argon atmospheric pressure and operated at 15-20 eV.

For sample solution: On $1\times1cm^2$ glass plates sample is dropcasted and kept at room temperature for solvent evaporation. The slides are sputtered with gold particles under argon atmospheric pressure and operated at 15-20 eV.

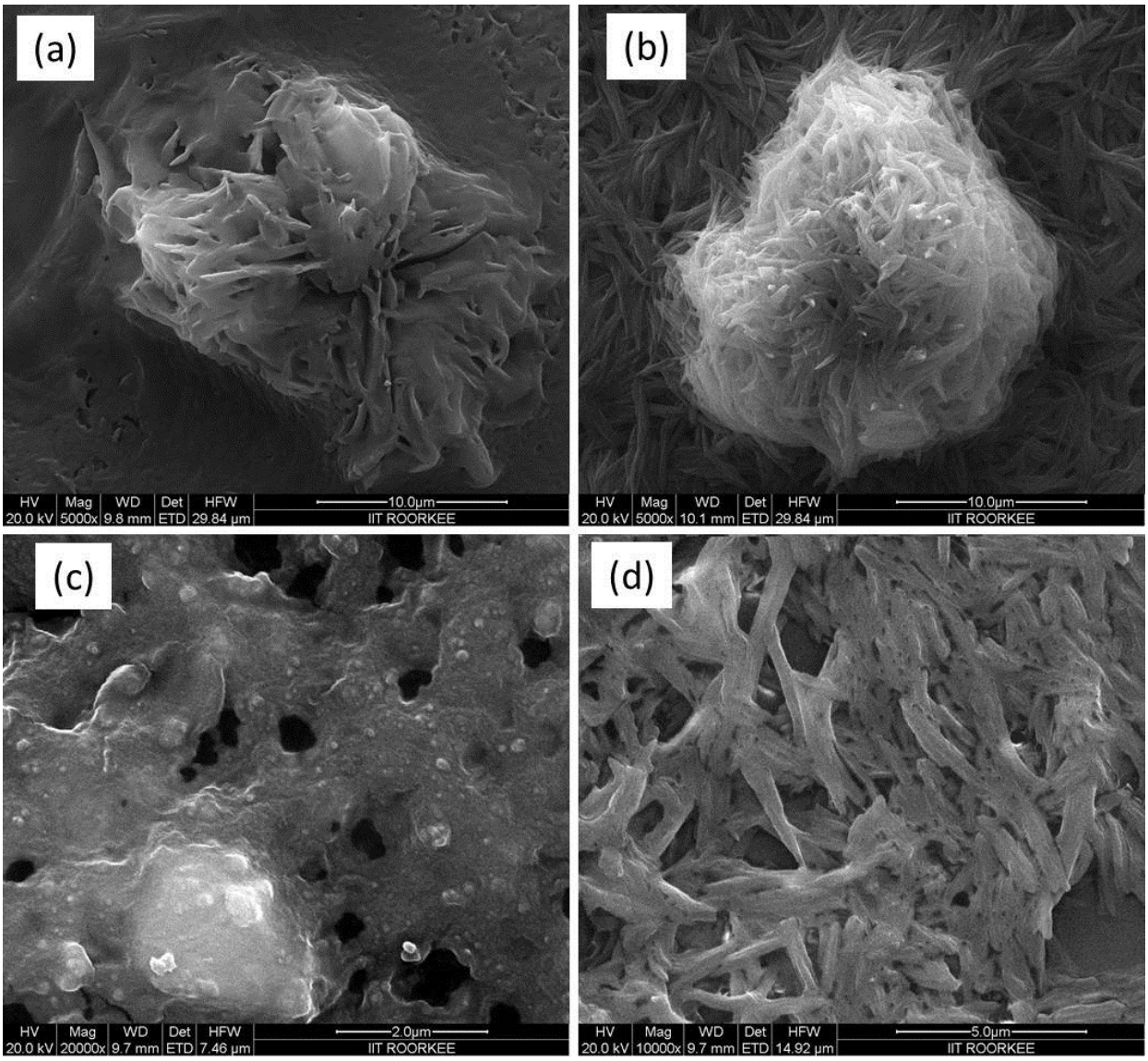

Fig. S8 FESEM images (**a-d**) of compounds **3a-3d** respectively showing formation of ill-defined aggregated cluster owing to poor control over concentration and aggregation, scale bar: 10, 10, 2, 4µm respectively.

Sample preparation for optical microscopy morphological studies:

The 1mM sample solution in DCM is drop casted on glass plates and evaporated at room temperature. The fluorescence images are captured from the slides observed under excitation using blue and green light.

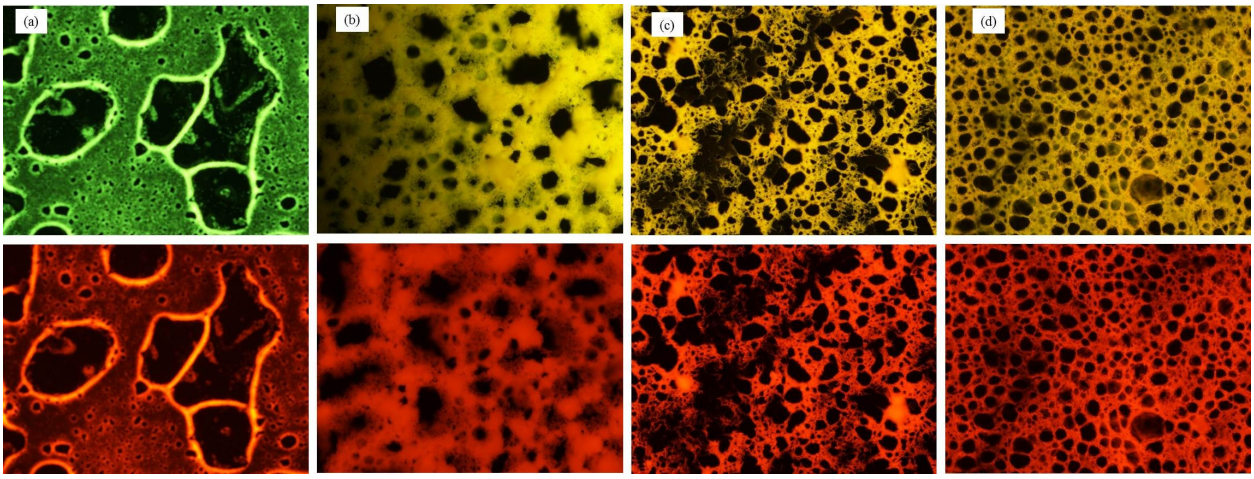

Fig. S9 Fluorescence microscopy images of the dyes (**a-d**) **3a-3d** respectively obtained from dichloromethane solution (1mM), above row under excitation by blue light (450-490 nm), below row under green light (510-550 nm).

Table S1 Absorption and emission data of the dyes **3a-3d** recorded in THF solutions, thin film and solid state.

Dyes	λ_{max}, nm (ε_{max}, M^{-1} cm^{-1} × 10^3)		λ_{em}, nm (Φ_F %)		
	THF	Thin film	THF	Thin film	Solid
3a	420 (41.9), 389 (50.3), 369 (32.5)	441, 408, 384	434, 462	519, 547	534 (05)
3b	439 (17.0),s 395 (49.2), 289 (28.4)	524, 483, 429	511, 540	554	578 (01)
3c	462 (40.6), 438 (45.2), 376 (17.1),s 354 (15.5), 328 (14.8), 279 (14.7)	494, 460	489, 517	566	592 (31)
3d	469 (25.2), 445 (25.6), 421 (24.6), 398 (22.7), 302 (20.8)	504, 471, 447, 416	502, 532	532, 565	589 (24)

Table S2 Time-resolved fluorescence spectroscopy data for the dyes in THF and 90% water - THF mixtures.

Dye	A_1	τ_1, ns	τ_a, ns	A_2	τ_2, ns	τ_b, ns	A_3	τ_3, ns	τ_c, ns	τ_{avg}, ns	χ^2
3a Sol.	0.66	0.99	0.65	0.34	3.17	1.08	-	-	-	1.73	1.01
3a Agg.	0.26	0.28	0.07	0.46	1.69	0.78	0.28	5.67	1.58	2.43	0.97
3b Sol.	0.61	1.26	0.77	0.15	3.84	0.58	0.24	0.20	0.05	1.40	1.32
3b Agg.	0.001	0.85	0.001	0.00	2.43	0.00	0.99	0.01	0.01	0.01	1.40
3c Sol.	0.53	1.30	0.69	0.28	3.94	1.10	0.19	0.17	0.03	1.83	1.15
3c Agg.	0.00	1.64	0.00	0.00	4.08	0.00	1.00	0.01	0.01	0.01	1.44
3d Sol.	0.39	1.30	0.51	0.61	5.06	3.07	-	-	-	3.58	1.02
3d Agg.	0.73	0.89	0.65	0.27	4.43	1.19	-	-	-	1.84	0.97

Where τ_1/ τ_2 /τ_3, Life time of different decay channels from FLS experiment in ns using 405 nm as excitation wavelength; $A_1/A_2/A_3$, Contribution of different decay channels in solution; fitted by either double or triple exponential; χ^2, correlation of exponential fit; τ_{avg} = Fluorescence lifetime decay measured as $\tau_{avg} = (A_1 \times \tau_1) + (A_2 \times \tau_2) + (A_3 \times \tau_3)$ in ns.

Table S3 Data of DLS-determined size distribution by intensity for the aggregates formed from dyes in THF: H_2O (90 %, 2×10^{-5} M).

Dye	d_{avg}, nm	d_m, nm
3a	142.6	153.8
3b	151.4	130.8
3c	190.9	127.4
3d	179.4	154.4

Table S4 Calculated interplanar distances, d (Å) using Braggs equation ($n\lambda=2d\sin\theta$) from the peaks obtained in powder X-ray diffraction of the small molecules.

Dye	2θ (d, Å), d/4	2θ (d, Å), d/3	2θ (d, Å), d/2	2θ (d, Å), d
3a	25.46 (3.49)	14.22 (6.22)	10.06 (8.78)	-
3b	25.92 (3.43)	15.62 (5.66)	10.27 (8.60)	5.66 (15.59)
3c	25.02 (3.55)	16.61 (5.33)	11.01 (8.03)	6.33 (13.94)
3d	25.47 (3.49)	16.26 (5.44)	8.00 (11.04)	6.77 (13.04)

Table S5 Thermal analysis data of the naphthalimide based small molecules.

Dye	T_{onset}, °C[a]	T_d, °C	T_m,°C
3a	426	484, 582	199
3b	446	476, 643	296
3c	431	482, 669	272
3d	456	475, 620	286

[a]Decomposition temperature wrt 10% wt. loss

Table S6 Computed electronic parameters for the compounds by the TDDFT (M06-2x/6-31G(d,p)) method.

Dye	λ_{max}, nm	*f*	Composition
3a	390	1.49	HOMO → LUMO (91%)
3b	406	1.70	HOMO → LUMO (79%), HOMO-1 → LUMO+1 (7%)
	349	0.95	HOMO → LUMO+2 (63%), HOMO -1 → LUMO+1 (16%)
3c	446	1.81	HOMO → LUMO (93%)
	328	0.29	HOMO → LUMO+2 (77%), HOMO-1 → LUMO+1 (14%)
3d	436	1.62	HOMO → LUMO (92%)
	361	0.38	HOMO-1 → LUMO (52%), HOMO → LUMO+1 (24%), HOMO-3 → LUMO (10%)

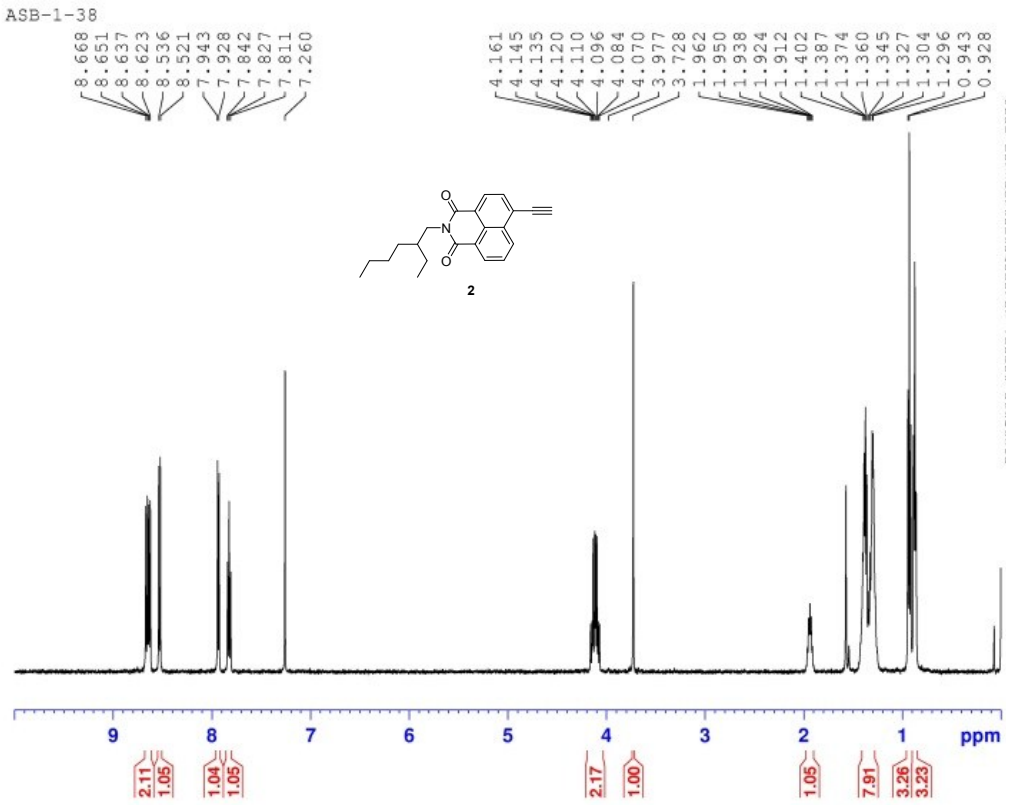

Fig. 10 ^{1}H NMR spectra of **2** in $CDCl_3$.

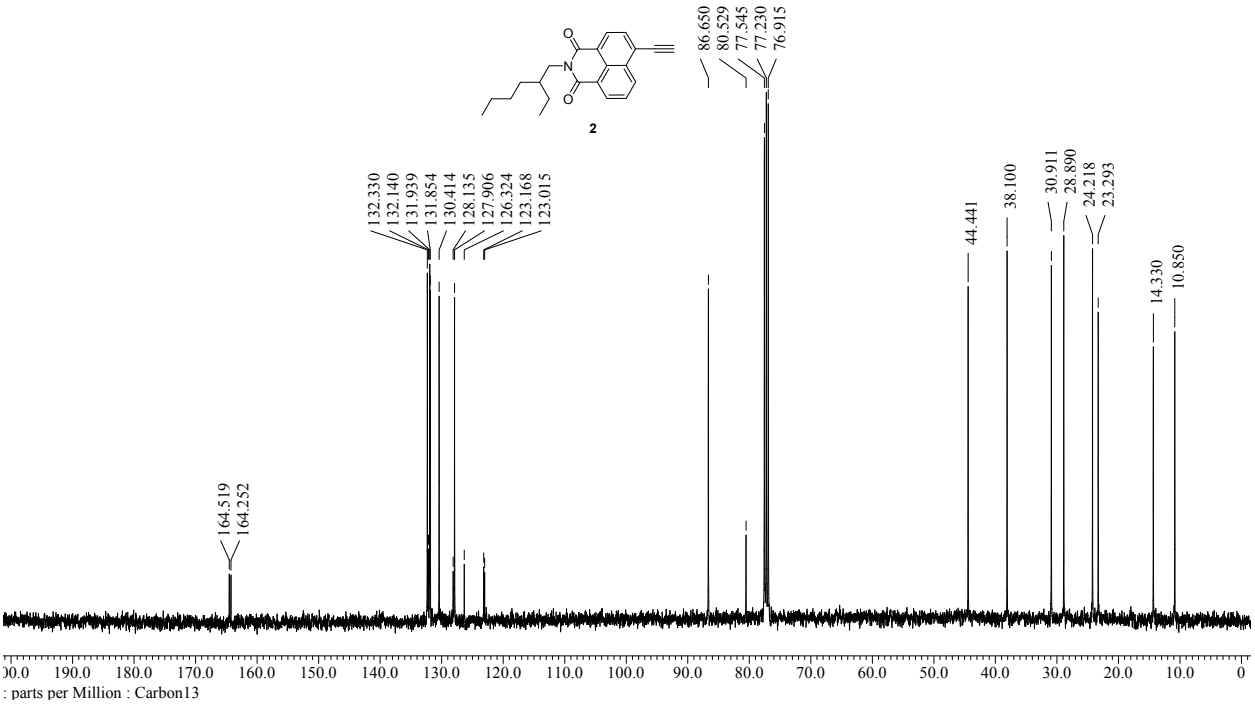

Fig. 11 ^{13}C NMR spectra of **2** in $CDCl_3$.

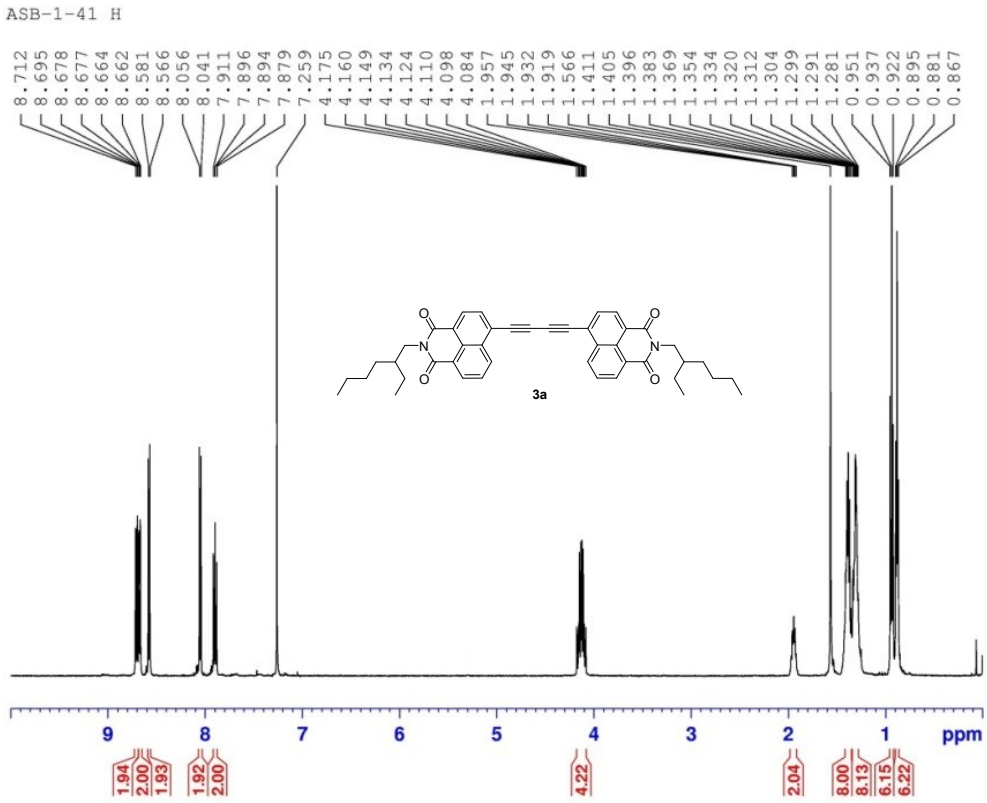

Fig. 12 ^{1}H NMR spectra of **3a** in $CDCl_3$.

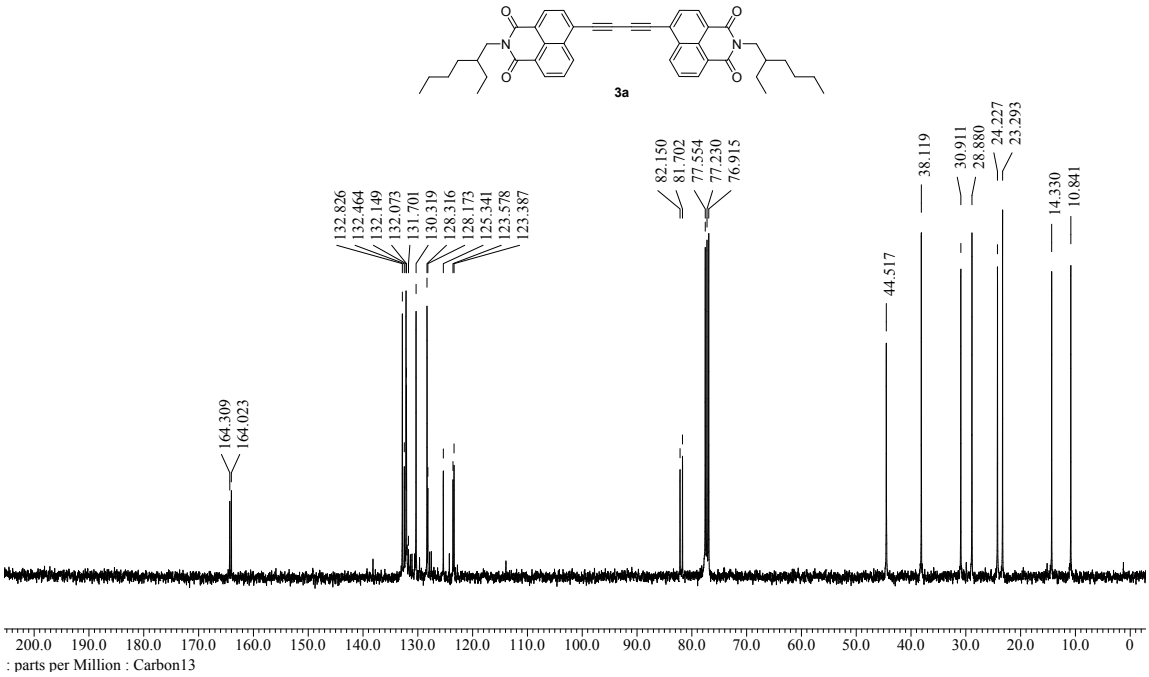

Fig. 13 ^{13}C NMR spectra of **3a** in $CDCl_3$.

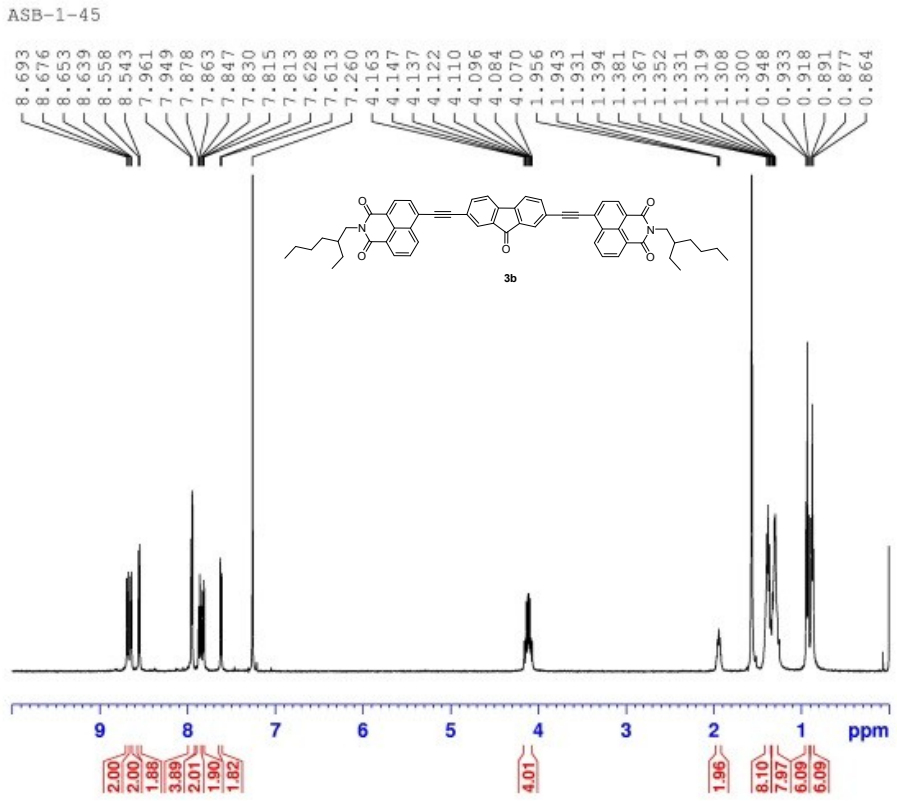

Fig. 14 ^{1}H NMR spectra of **3b** in $CDCl_3$.

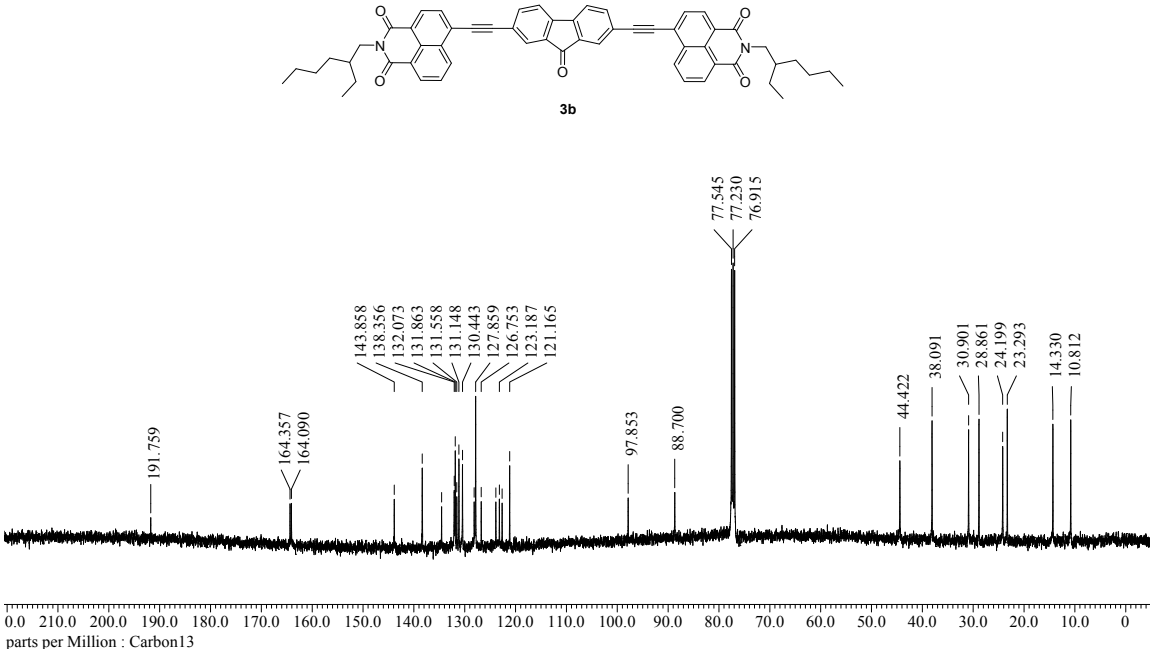

Fig. 15 ^{13}C NMR spectra of **3b** in $CDCl_3$.

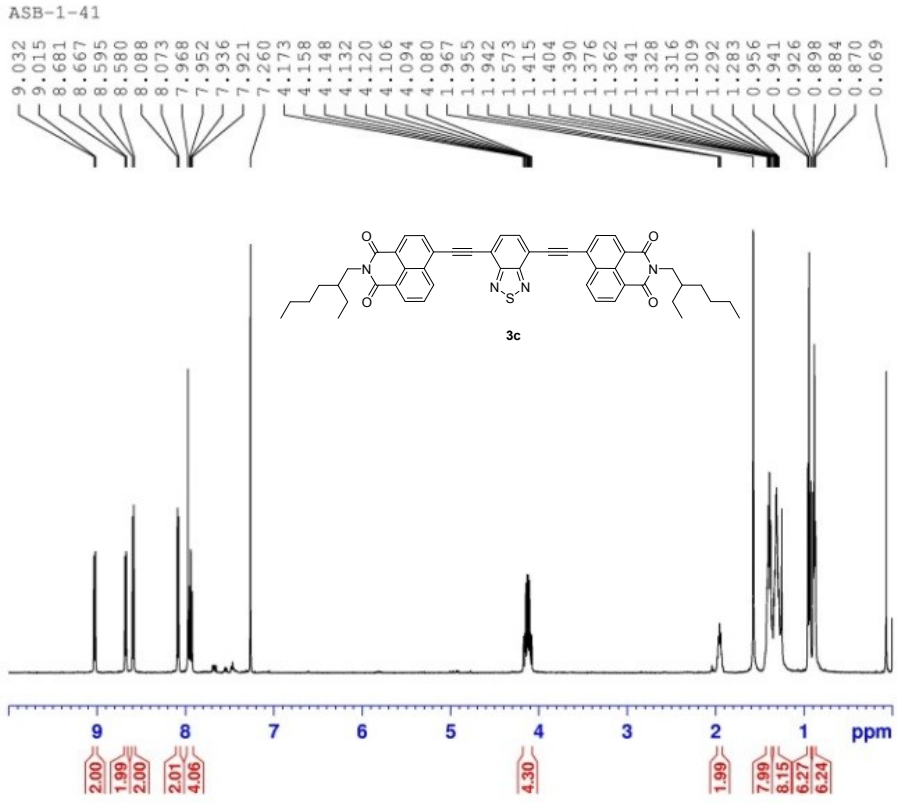

Fig. 16 ^{1}H NMR spectra of **3c** in $CDCl_3$.

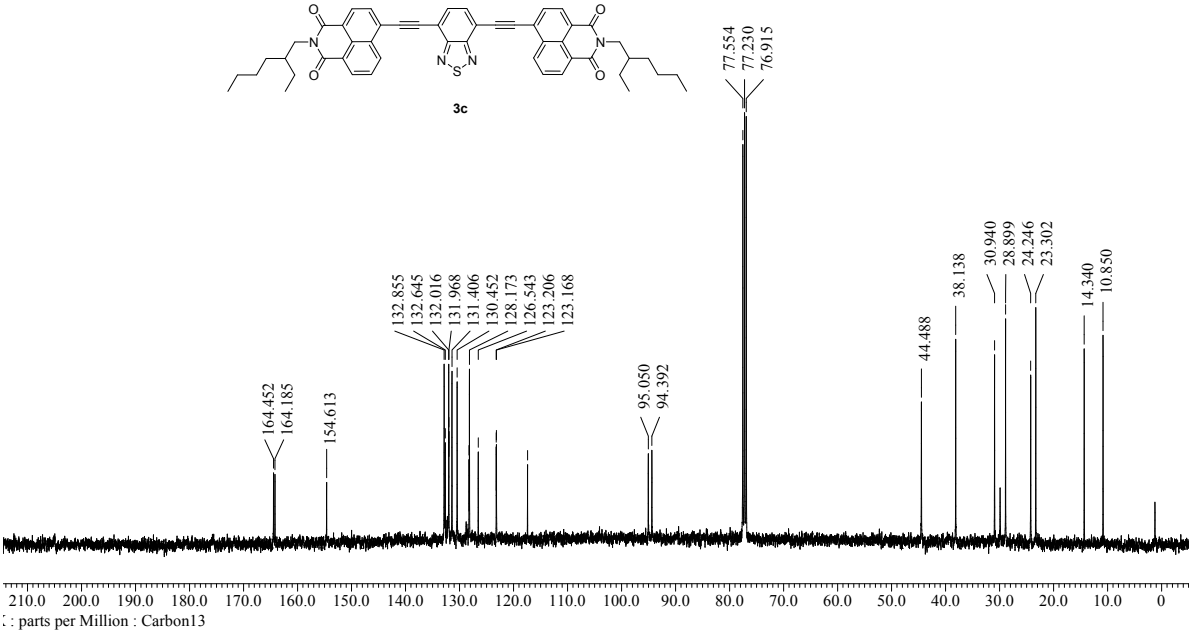

Fig. 17 ^{13}C NMR spectra of **3c** in $CDCl_3$.

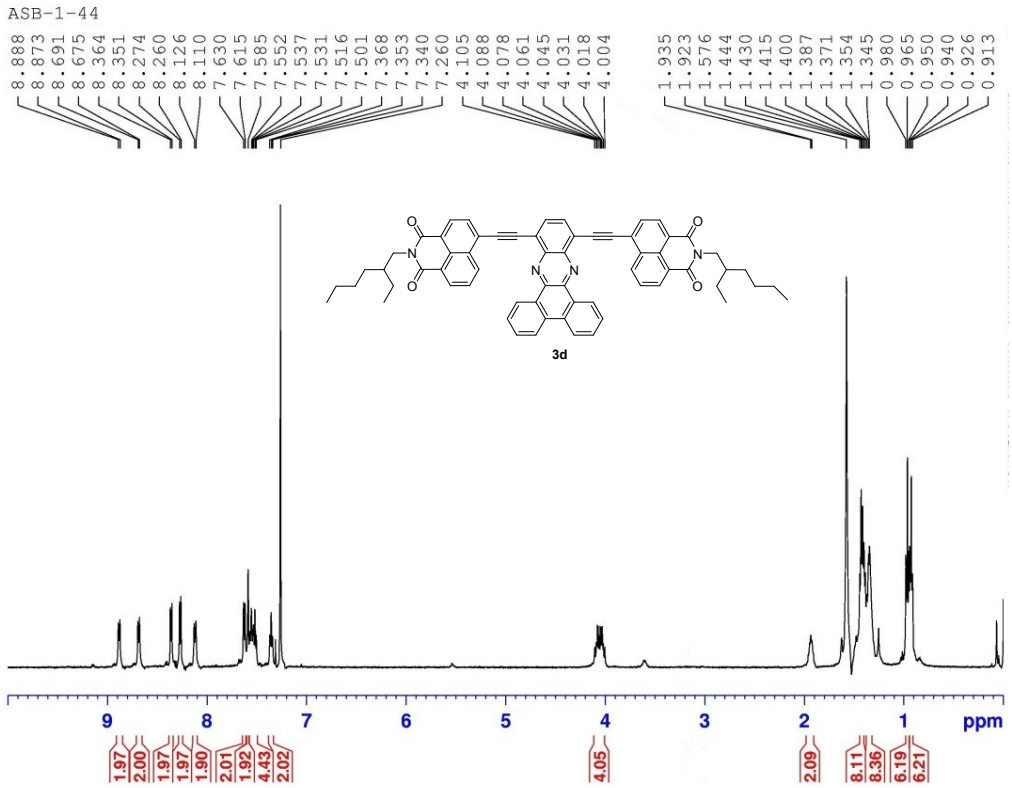

Fig. 18 ^{1}H NMR spectra of **3d** in $CDCl_3$.

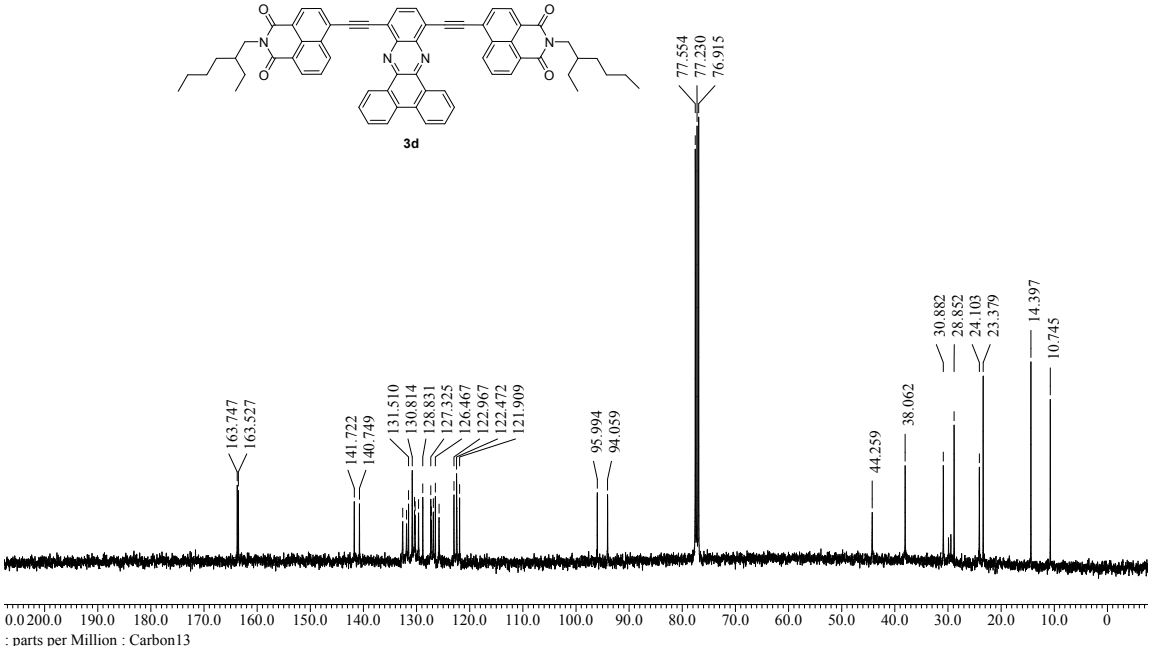

Fig. 19 ^{13}C NMR spectra of **3d** in $CDCl_3$.

Table S7 Cartesian coordinates for the optimized geometry of **3a**.

Energy = -1563.27069756 hartrees

Atom	X	Y	Z
C	6.143708	-2.57821	-0.000202
C	4.769229	-2.88723	-0.000198
C	3.823311	-1.88151	-0.000098
C	4.213994	-0.51991	0.000002
C	5.606713	-0.20891	-0.000007
C	6.560459	-1.25922	-0.000112
C	3.269122	0.566776	0.000114
C	3.733179	1.884182	0.00021
C	5.106111	2.167887	0.000201
C	6.035883	1.141809	0.000091
C	7.482379	1.471163	0.00008
C	8.01617	-0.96119	-0.000118
O	8.862514	-1.84417	-0.000155
N	8.379667	0.39584	-0.000098
O	7.898728	2.621929	0.0002
H	6.896458	-3.35888	-0.000273
H	4.453834	-3.9257	-0.000275

H	3.013318	2.695162	0.000291
H	5.463929	3.191603	0.000278
H	2.765104	-2.12143	-0.000093
C	9.805895	0.741047	-0.000124
H	10.04164	1.33661	-0.884395
H	10.04202	1.335441	0.884841
H	10.37095	-0.1873	-0.000824
C	1.875177	0.313629	0.000117
C	0.669157	0.110964	0.00013
C	-0.66916	-0.111	0.000138
C	-1.87518	-0.31366	0.000144
C	-3.26913	-0.5668	0.000134
C	-3.73319	-1.8842	0.000224
C	-4.21399	0.519902	0.000021
C	-5.10613	-2.16789	0.000203
H	-3.01334	-2.69518	0.000307
C	-5.60671	0.208908	0
C	-3.8233	1.881494	-0.000071
C	-6.03589	-1.14181	0.000094
H	-5.46395	-3.19161	0.000273
C	-6.56045	1.259229	-0.00011
C	-4.76921	2.887226	-0.000174
H	-2.76509	2.121404	-0.000057
C	-7.48239	-1.47115	0.000071
C	-6.14369	2.578212	-0.000194
C	-8.01617	0.961213	-0.000141
H	-4.45381	3.925689	-0.00024
O	-7.89875	-2.62191	0.000153
N	-8.37967	-0.39582	-0.00005
H	-6.89644	3.358887	-0.000278
O	-8.8625	1.844201	-0.000242
C	-9.80589	-0.74103	-0.000077
H	-10.371	0.187316	-0.00005
H	-10.0418	-1.33599	-0.884717
H	-10.0418	-1.33606	0.884513

Table S8 Cartesian coordinates for the optimized geometry of **3b**.

Energy = -2137.52295062 hartrees

Atom	X	Y	Z
C	-10.4978	2.419238	0
C	-9.14436	2.80916	0.000004
C	-8.14129	1.860466	0.000029
C	-8.44883	0.477736	0.000046

C	-9.82096	0.08528	0.00005
C	-10.8351	1.077606	0.000021
C	-7.43955	-0.54872	0.000053
C	-7.82529	-1.89035	0.000082
C	-9.17894	-2.256	0.000097
C	-10.1696	-1.28854	0.000079
C	-11.5926	-1.70301	0.000103
C	-12.2705	0.693888	0.00001
O	-13.1682	1.525261	-4.5E-05
N	-12.5526	-0.68192	0.000042
O	-11.9422	-2.87598	0.000153
H	-11.296	3.153368	-2.4E-05
H	-8.8911	3.864592	-8E-06
H	-7.05875	-2.6574	0.00009
H	-9.47417	-3.29955	0.000121
H	-7.09891	2.16126	0.000034
C	-13.9554	-1.11177	0.000031
H	-14.1552	-1.72023	-0.88435
H	-14.1553	-1.72002	0.884537
H	-14.5754	-0.21914	-9.1E-05
C	-6.05998	-0.21252	0.000038
C	-4.87235	0.057543	-3.5E-05
C	-3.48062	0.346353	-7.5E-05
C	-3.02558	1.683538	-0.00027
C	-2.53168	-0.70429	0.000075
C	-1.66443	1.995414	-0.00033
H	-3.75996	2.48221	-0.00039
C	-1.18923	-0.38193	0.000015
H	-2.85243	-1.74073	0.000226
C	-0.73834	0.955622	-0.00018
H	-1.34836	3.034179	-0.00048
C	-3E-06	-1.29745	0.000137
C	0.738349	0.955618	-0.00019
C	1.189226	-0.38194	0.000005
C	1.664442	1.995406	-0.00037
C	2.531678	-0.7043	0.000033
C	3.025592	1.683525	-0.00035
H	1.348378	3.034173	-0.00054
C	3.480623	0.346338	-0.00015
H	2.852422	-1.74074	0.000182
H	3.759972	2.482194	-0.00051
O	-6E-06	-2.51377	0.000303
C	4.872349	0.05752	-0.00013

C	6.059979	-0.21257	-0.00011
C	7.439554	-0.54876	-9.3E-05
C	8.448822	0.477708	0.000047
C	7.825313	-1.89039	-0.00022
C	8.141266	1.860434	0.000187
C	9.820954	0.085271	0.000052
C	9.178964	-2.25602	-0.00022
H	7.058779	-2.65745	-0.00033
C	9.144322	2.809141	0.000332
H	7.098877	2.161213	0.000184
C	10.83508	1.077612	0.000204
C	10.1696	-1.28854	-9.2E-05
H	9.474217	-3.29956	-0.00033
C	10.4978	2.419239	0.000342
H	8.891045	3.864571	0.000437
C	12.27053	0.693913	0.000229
C	11.59264	-1.70299	-0.00012
H	11.296	3.153381	0.00046
O	13.16816	1.525297	0.000426
N	12.5526	-0.68189	-1.2E-05
O	11.94219	-2.87596	-0.00025
C	13.95543	-1.11172	-3.1E-05
H	14.15525	-1.7201	0.884396
H	14.15523	-1.72006	-0.88449
H	14.57539	-0.21908	-1.9E-05

Table S9 Cartesian coordinates for the optimized geometry of **3c**.

Energy = -2440.99887495 hartrees

Atom	X	Y	Z
C	3.566836	5.297888	-0.00038
C	2.855504	4.110367	-0.0004
C	1.448224	4.113765	-0.0002
C	0.73642	5.340679	0.000013
C	1.487686	6.533692	0.000094
C	2.874338	6.516364	-0.0001
C	0.718764	2.846782	-0.00015
C	-0.73647	5.340672	0.000119
C	-1.44826	4.113749	0.000133
C	-0.71879	2.846773	-1.6E-05
C	-2.85554	4.110338	0.000254
H	-3.35925	3.150688	0.000268
C	-3.56689	5.297851	0.000344
C	-2.8744	6.516335	0.000292

C	-1.48775	6.533677	0.000178
H	4.652399	5.285599	-0.00056
H	3.359225	3.150724	-0.00057
H	0.98416	7.49284	0.000336
H	3.421884	7.454145	-3.4E-05
H	-4.65245	5.285549	0.000439
H	-3.42196	7.45411	0.000334
H	-0.98423	7.49283	0.000108
N	1.402086	1.707944	-0.00022
N	-1.4021	1.707929	-3.7E-05
C	0.715689	0.548985	-0.00022
C	-0.71569	0.548979	-0.00016
C	1.434218	-0.6997	-0.00028
C	-1.43421	-0.69972	-0.00025
C	0.701419	-1.88513	-0.00034
H	1.231959	-2.83106	-0.00039
C	-0.7014	-1.88514	-0.00034
H	-1.23193	-2.83108	-0.00041
C	2.850055	-0.71991	-0.00027
C	4.067428	-0.76961	-0.00018
C	5.485482	-0.79694	-0.00012
C	6.199785	-2.04737	0.00002
C	6.20273	0.401396	-0.00019
C	5.548822	-3.30517	0.000129
C	7.626616	-2.01895	0.000066
C	7.604359	0.408639	-0.00015
H	5.656363	1.337987	-0.00028
C	6.275699	-4.47909	0.000281
H	4.464195	-3.32808	0.000089
C	8.353221	-3.2376	0.000223
C	8.315153	-0.78012	-2.8E-05
H	8.157417	1.341563	-0.00021
C	7.683809	-4.44834	0.000334
H	5.76083	-5.43459	0.000372
C	9.838785	-3.23387	0.000285
C	9.796575	-0.74316	0.000004
H	8.267645	-5.36226	0.000471
O	10.49415	-4.26712	0.000445
N	10.46352	-1.97577	0.000154
O	10.43459	0.301618	-4.5E-05
C	11.92953	-1.91991	0.000206
H	12.27896	-1.38297	-0.88403
H	12.279	-1.38383	0.884966

H	12.29922	-2.94189	-0.00024
C	-2.85004	-0.71993	-0.00023
C	-4.06742	-0.76961	-9.6E-05
C	-5.48547	-0.79694	-2.7E-05
C	-6.19977	-2.04737	-0.00011
C	-6.20273	0.4014	0.000146
C	-5.5488	-3.30517	-0.0003
C	-7.6266	-2.01896	-1.7E-05
C	-7.60436	0.408633	0.000237
H	-5.65636	1.337992	0.000207
C	-6.27567	-4.47909	-0.0004
H	-4.46417	-3.32806	-0.00037
C	-8.3532	-3.23762	-0.00011
C	-8.31514	-0.78014	0.000157
H	-8.15742	1.341553	0.000364
C	-7.68378	-4.44835	-0.0003
H	-5.76079	-5.43459	-0.00056
C	-9.83876	-3.23389	0.000008
C	-9.79657	-0.74319	0.000255
H	-8.26761	-5.36227	-0.00037
O	-10.4941	-4.26715	0.000017
N	-10.4635	-1.9758	0.000144
O	-10.4346	0.30159	0.00043
C	-11.9295	-1.91995	0.000267
H	-12.2789	-1.38343	0.884784
H	-12.2791	-1.38346	-0.88421
H	-12.2992	-2.94193	0.000304

Table S10 Cartesian coordinates for the optimized geometry of **3d**.

Energy = -2300.79588315 hartrees

Atom	X	Y	Z
C	7.879393	-3.05205	-0.03046
C	6.474351	-3.15158	-0.03594
C	5.690832	-2.01479	-0.02431
C	6.279811	-0.72678	-0.00674
C	7.703293	-0.62846	-0.00255
C	8.4882	-1.81006	-0.01525
C	5.50741	0.487803	0.006933
C	6.163133	1.720736	0.025254
C	7.56312	1.795627	0.031411
C	8.330551	0.642579	0.016496
C	9.809793	0.75382	0.024686
C	9.971302	-1.73123	-0.00984

O	10.68067	-2.728	-0.00547
N	10.53519	-0.44583	-0.01473
O	10.38909	1.83129	0.05931
H	8.507531	-3.93608	-0.03842
H	6.00689	-4.13104	-0.04904
H	5.570463	2.628802	0.035658
H	8.069738	2.754312	0.04769
H	4.608658	-2.09162	-0.02811
C	11.99887	-0.34038	-0.01629
H	12.28499	0.528548	-0.60644
H	12.37557	-0.21092	1.002784
H	12.40437	-1.2588	-0.43421
C	4.089941	0.448505	0.002855
C	2.871713	0.442485	0.001317
C	1.459127	0.450195	-0.00051
C	0.724489	1.690028	-0.00146
C	0.706464	-0.71901	-0.00107
N	1.260443	2.912756	-0.00074
C	-0.72474	1.690076	-0.00293
C	-0.70661	-0.71898	-0.00214
H	1.225676	-1.67131	-0.00035
S	-6.2E-05	3.968223	-0.0029
N	-1.26064	2.91283	-0.00424
C	-1.45933	0.450198	-0.00315
H	-1.22583	-1.67128	-0.00229
C	-2.87189	0.442634	-0.00422
C	-4.09013	0.449485	-0.00656
C	-5.50759	0.488392	-0.00901
C	-6.27972	-0.72637	0.004232
C	-6.16355	1.721212	-0.02499
C	-5.69042	-2.01428	0.018796
C	-7.70321	-0.62833	0.00279
C	-7.56355	1.795823	-0.02856
H	-5.57104	2.629385	-0.03537
C	-6.47369	-3.15124	0.030231
H	-4.60821	-2.09087	0.020426
C	-8.48785	-1.8101	0.015427
C	-8.33075	0.642608	-0.01351
H	-8.07037	2.754434	-0.04279
C	-7.87876	-3.05199	0.027694
H	-6.00599	-4.13062	0.04091
C	-9.97097	-1.73152	0.013129
C	-9.81003	0.753602	-0.01857

H	-8.50671	-3.93616	0.035627
O	-10.6802	-2.72836	0.008961
N	-10.5351	-0.44624	0.020759
O	-10.3895	1.831024	-0.05101
C	-11.9988	-0.34135	0.02535
H	-12.2838	0.528609	0.614486
H	-12.3778	-0.21405	-0.99314
H	-12.4032	-1.2591	0.445867