Deep-blue emitting pyrene-benzimidazole conjugates for solution processed organic light-emitting diodes

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Electronic Supplementary Information

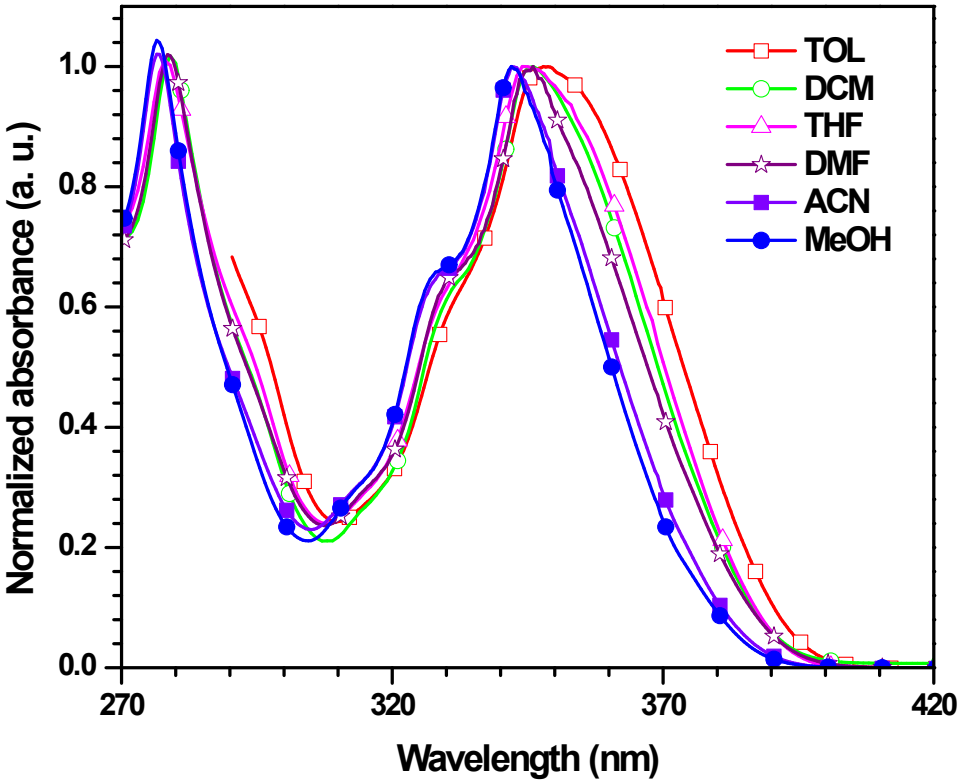

Fig. S1 Absorption spectra of **3a** recorded in different solvents.

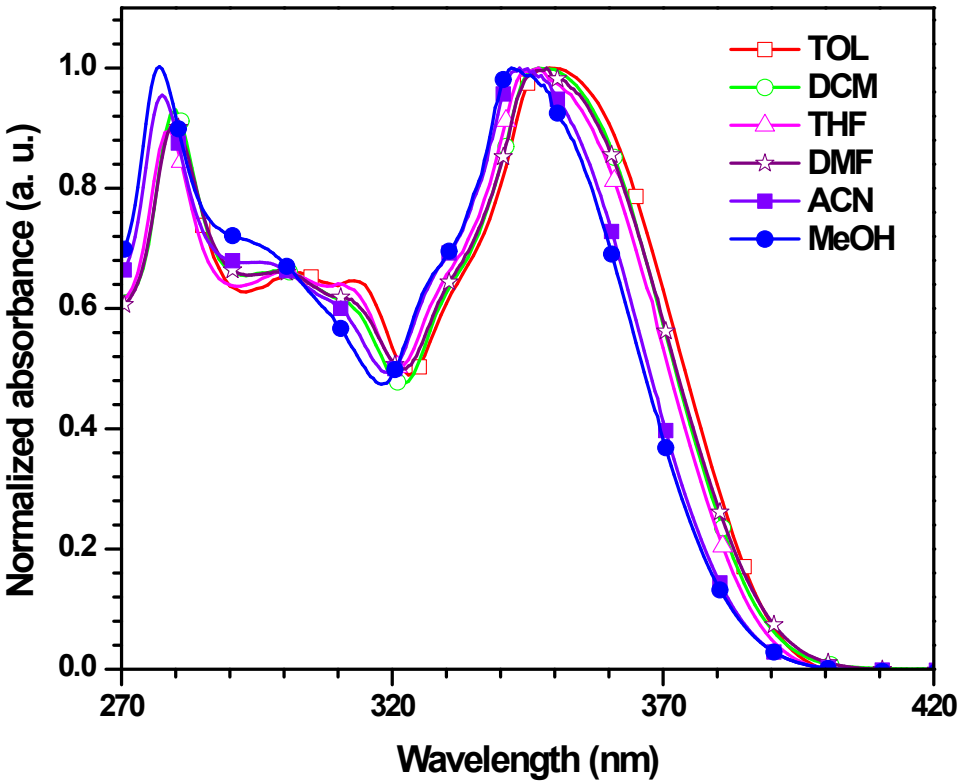

Fig. S2 Absorption spectra of **3b** recorded in different solvents.

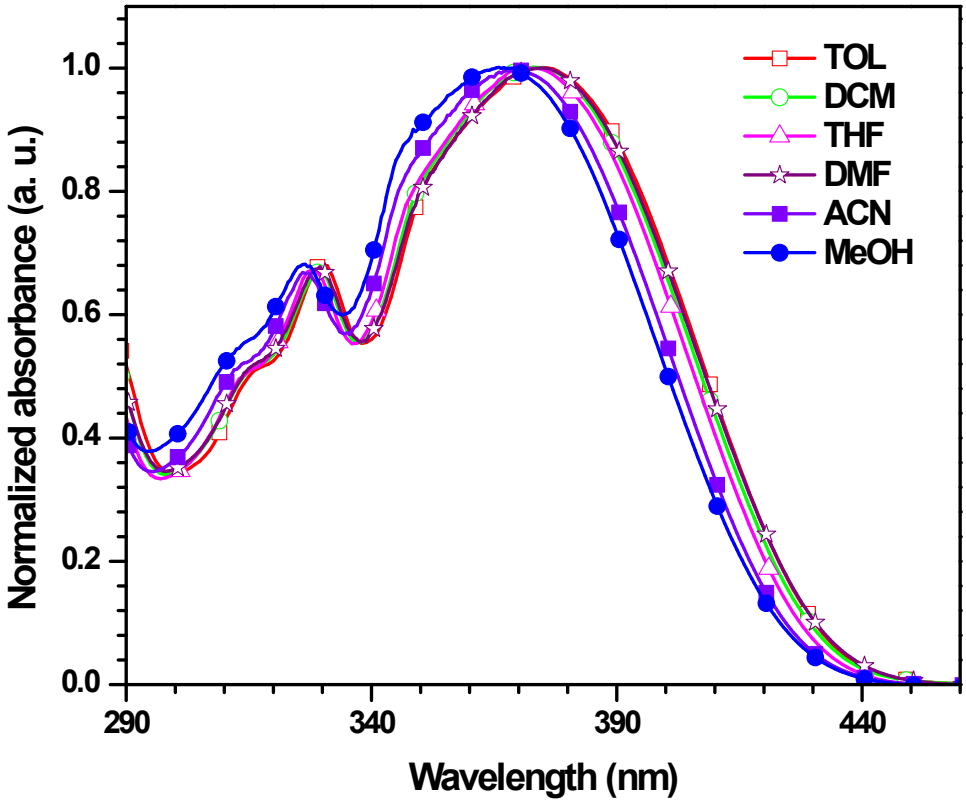

Fig. S3 Absorption spectra of **3c** recorded in different solvents.

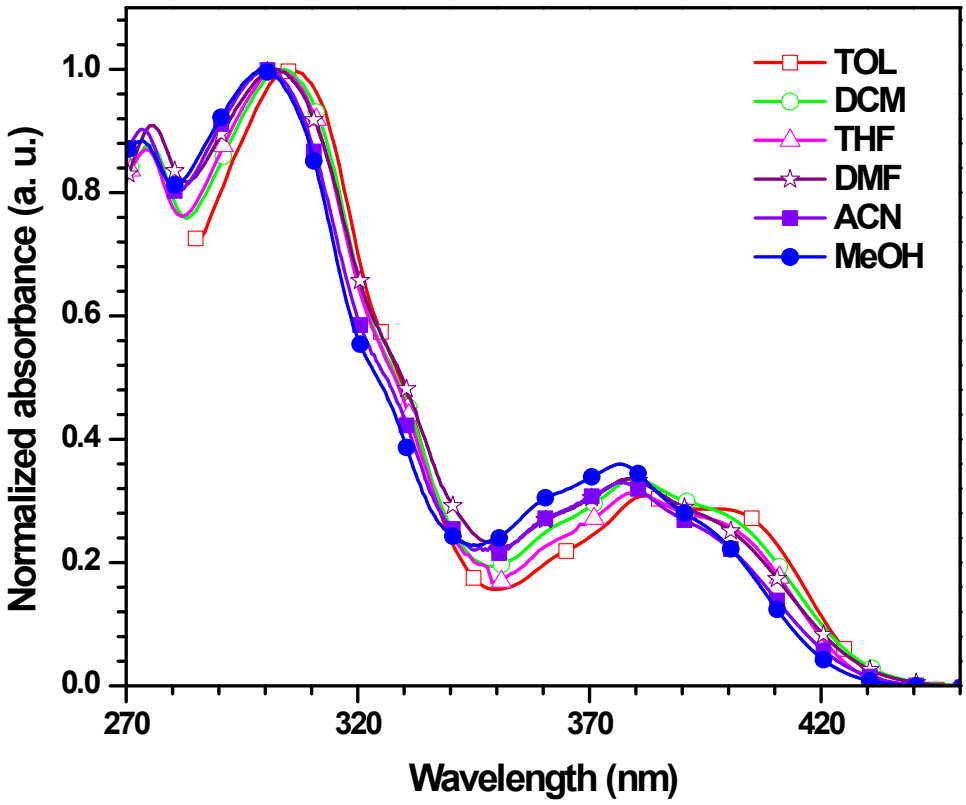

Fig. S4 Absorption spectra of **3d** recorded in different solvents.

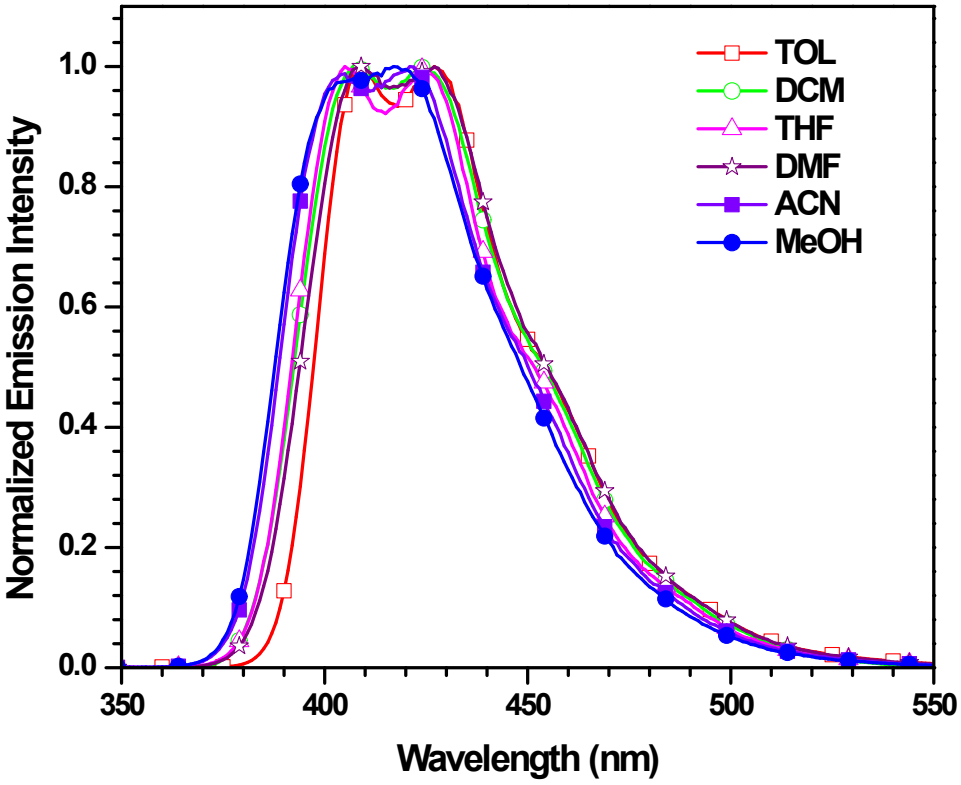

Fig. S5 Emission spectra of **3a** recorded in different solvents.

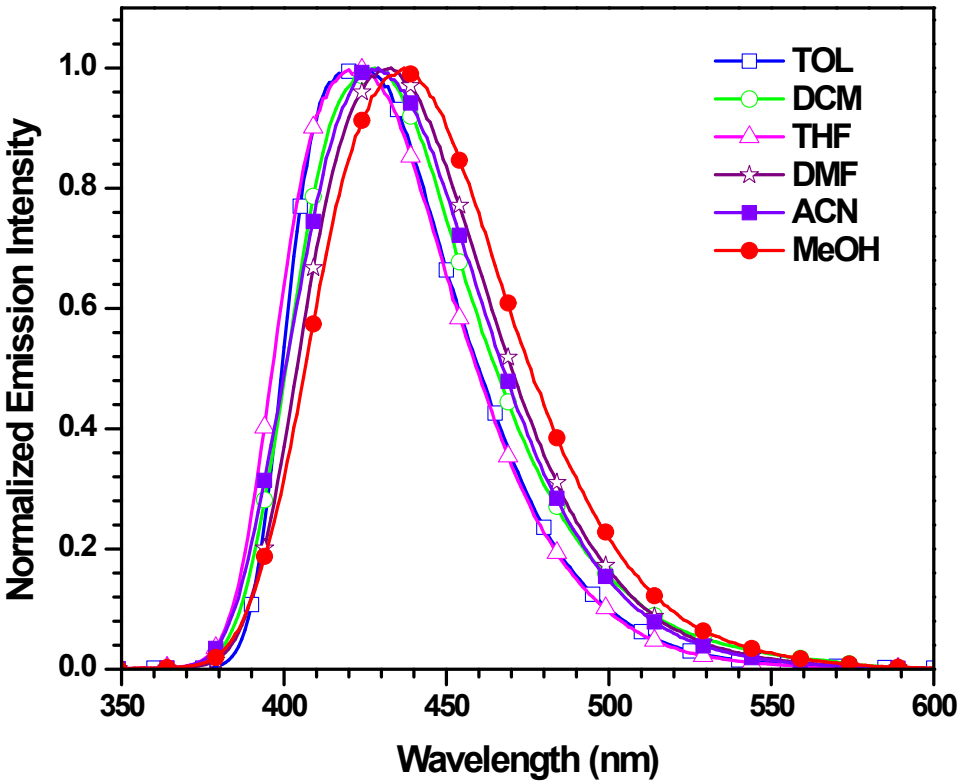

Fig. S6 Emission spectra of **3b** recorded in different solvents.

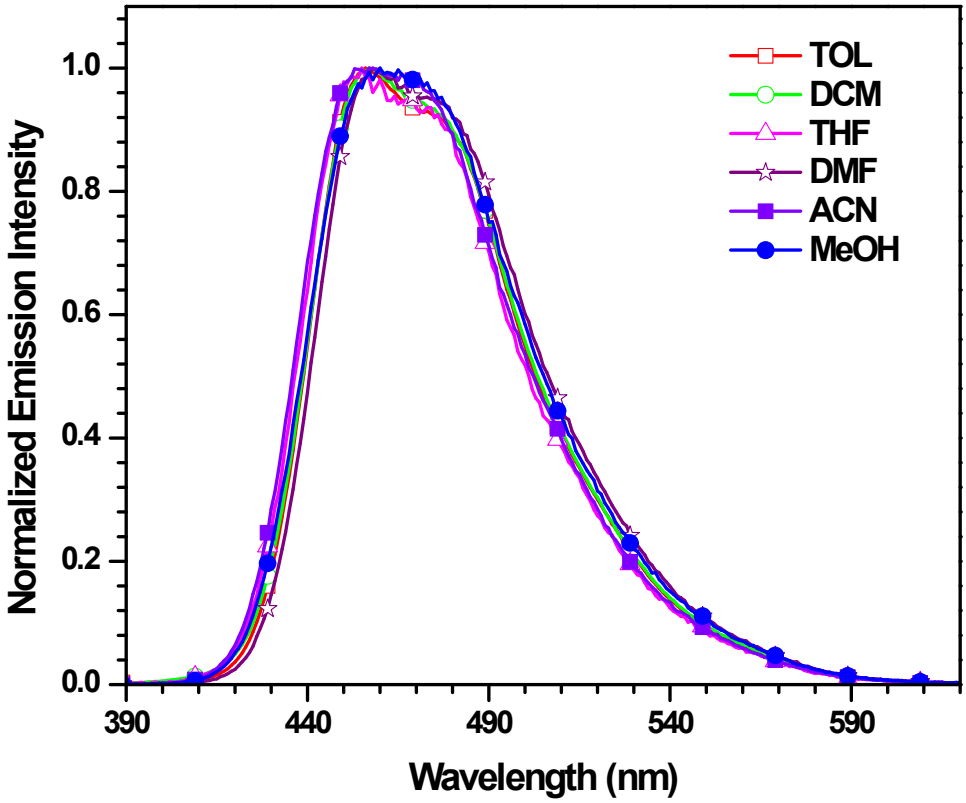

Fig. S7 Emission spectra of **3c** recorded in different solvents.

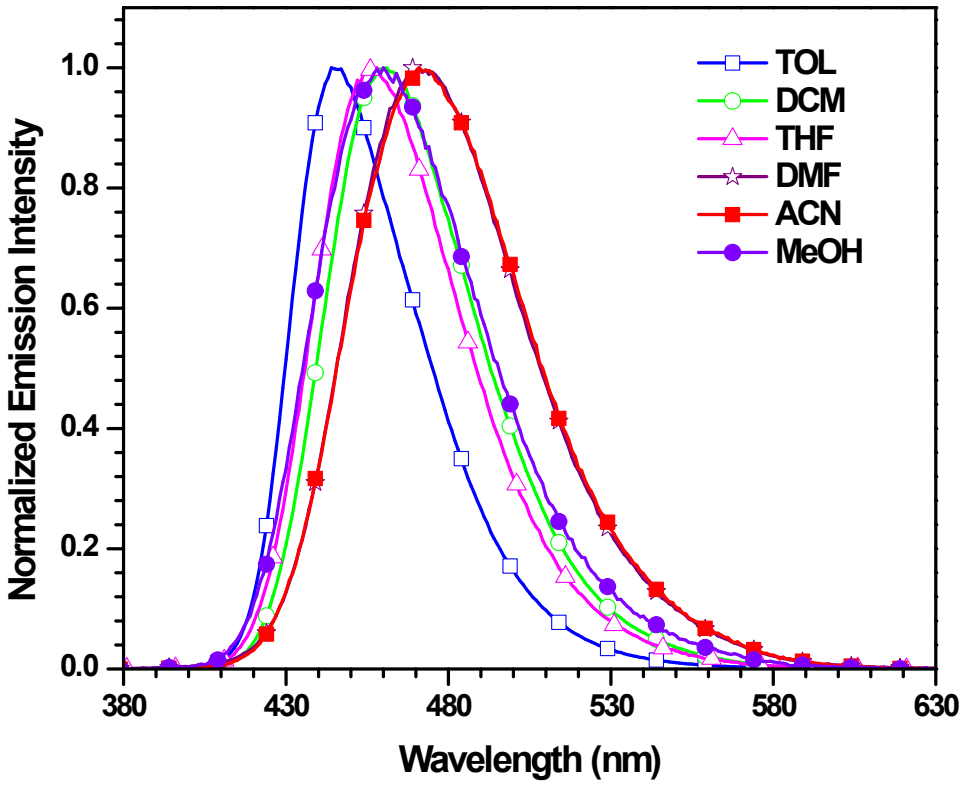

Fig. S8 Emission spectra of **3d** recorded in different solvents.

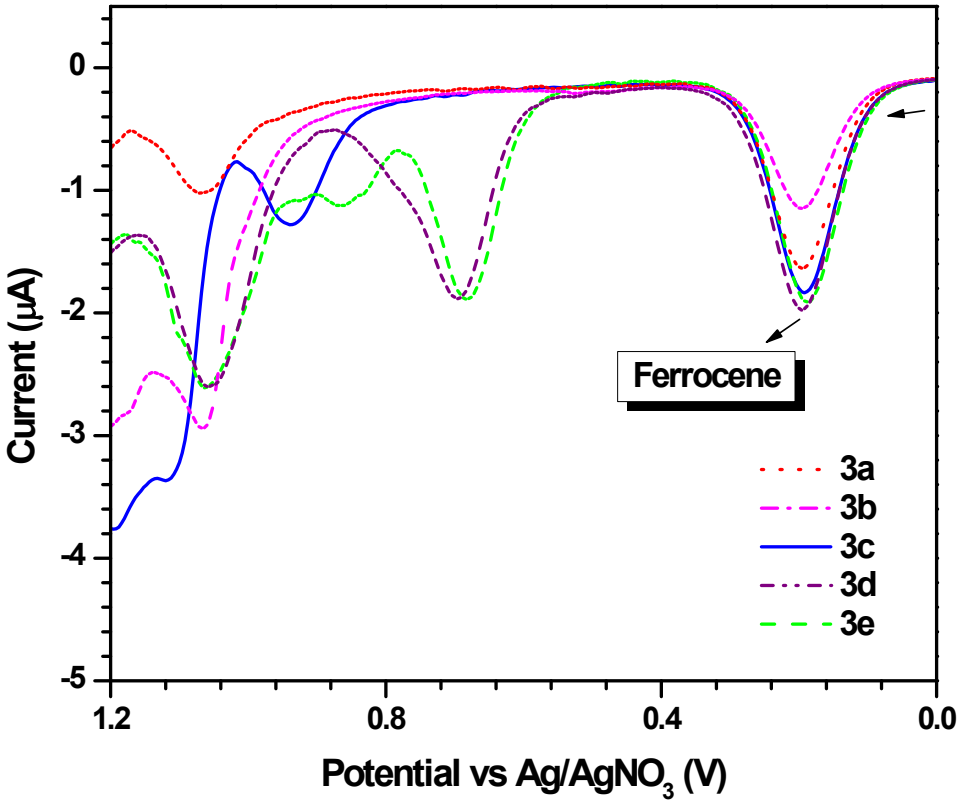

Fig. S9 Differential pulse voltammetry spectra of all dyes recorded in DCM.

Table S1 Solvatochromic data for the dyes.

Dye	λ_{abs} (nm)				λ_{em} (nm)				Stokes shift (cm^{-1})				FWHM (nm)			
	THF	DMF	ACN	MeOH	THF	DMF	ACN	MeOH	THF	DMF	ACN	MeOH	THF	DMF	ACN	MeOH
3a	278, 344	279, 346	277, 342	277, 342	405, 424	408, 427	405, 421	404, 417	4378	4452	4548	4487	57	58	58	58
3b	279, 300, 347	280, 348	278, 344	277, 342	423	433	429	437	5178	5641	5844	6356	61	65	66	69
3c	272, 328, 372	279, 330, 375	277, 326, 369	276, 327, 366	455	458	457	460	4904	4833	5218	5361	64	65	64	65
3d	274, 302, 380	278, 303, 379	274, 301, 377	274, 300, 377	458	469	471	460	4482	5063	5294	4786	53	63	63	60
3e	274, 330, 380	275, 330, 379	273, 328, 378	272, 328, 377	464	483	483	463	4764	5681	5751	4857	55	66	67	62

Table S2 Dipole moment data for the dyes.

Dye	Onsager radius[a]	μ_g[a]	μ_e[b]
3a	5.69	3.54	-[c]
3b	6.08	3.60	7.52
3c	6.34	4.39	-[c]
3d	6.28	3.62	10.84
3e	6.24	3.66	12.00

[a] Calculated (B3LYP/6-31G). [b] Calculated following procedure in ref. 1.

[c] could not me calculated due to no significant variation in emission energy with solvent polarity.

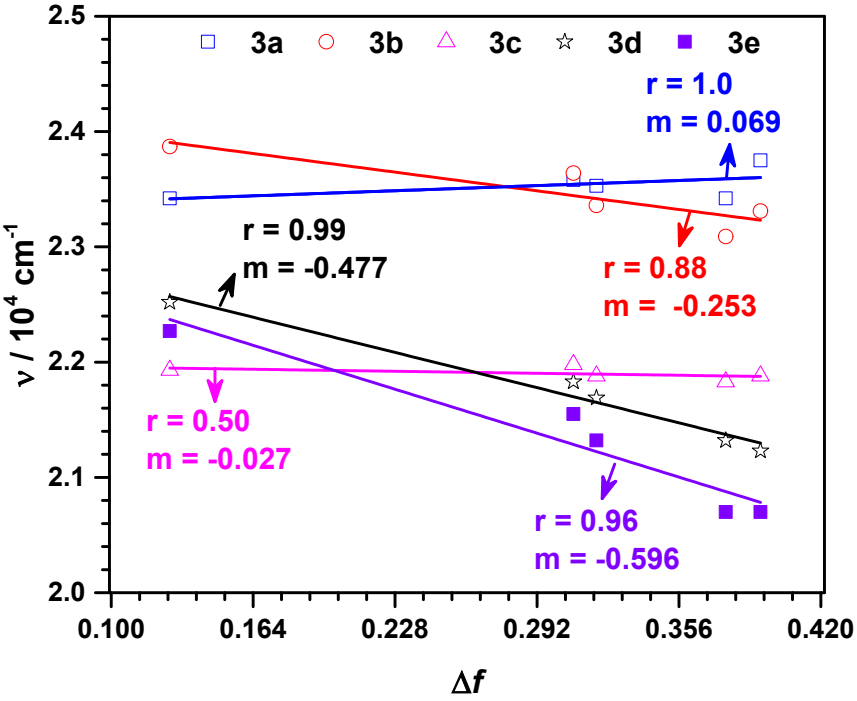

Fig. S10 Correlation plot of ν with Δf for the dyes **3a**-**3e**.

1. G. F. Mes, B. De Jong, H. J. Van Ramesdonk, J. W. Verhoeven, J. M. Warman, M. P. De Haas and L. E. W. Horsman-Van den Dool, *J. Am. Chem. Soc.*, 1984, **106**, 6524.

Table S3 Cartesian coordinates for the optimized structure **3a**.

Energy: -1225.52658127 hartrees

Atom	X	Y	Z
C	-6.11014	-1.36623	0.99295
C	-6.08833	-0.15013	0.31293
C	-4.88117	0.38602	-0.16325
C	-3.6647	-0.33136	0.05679
C	-3.69878	-1.57508	0.75532
C	-4.92987	-2.07253	1.21293
C	-4.82784	1.63683	-0.86706
C	-2.42221	0.19308	-0.41647
C	-2.40964	1.4428	-1.10871
C	-3.64698	2.14039	-1.3184
C	-1.1847	1.95082	-1.5655
H	-1.1669	2.89391	-2.10445
C	-0.00306	1.25995	-1.3431
C	0.01672	0.03097	-0.664
C	-1.20385	-0.52763	-0.1963
C	-1.27592	-1.77703	0.51474
C	-2.46227	-2.27056	0.96491
H	-2.48749	-3.21775	1.49736
H	-0.36167	-2.33656	0.6623
H	-5.75636	2.17663	-1.03306
H	-7.05345	-1.76565	1.35358
H	-7.01181	0.39709	0.14378
H	-4.95144	-3.02045	1.74376
H	-3.61882	3.08779	-1.84998
H	0.92781	1.67083	-1.71779
C	1.307	-0.66305	-0.48752
N	1.51254	-1.94143	-0.72574
N	2.483	0.00533	-0.11491
C	2.86029	-2.15671	-0.50743
C	3.49429	-0.95401	-0.12357
C	2.63847	1.34085	0.3646
C	3.60437	-3.33948	-0.61019
C	4.85415	-0.89325	0.18914
C	3.56488	2.19022	-0.25031
C	1.89022	1.79047	1.4575
H	3.12007	-4.26332	-0.90896
C	4.9613	-3.28492	-0.31337
C	5.57518	-2.08004	0.0842
H	5.32841	0.0308	0.5015
H	4.13237	1.83246	-1.10329
C	3.74115	3.48751	0.2315
C	2.0616	3.09345	1.92194

H	1.18145	1.12067	1.93204
H	5.56276	-4.18618	-0.38425
H	6.6362	-2.07575	0.31529
H	4.46167	4.14362	-0.24742
C	2.98819	3.94335	1.31456
H	1.47546	3.44106	2.76715
H	3.12281	4.95528	1.68405

Table S4 Cartesian coordinates for the optimized structure **3b**.

Energy: -1456.59000724 hartrees

Atom	X	Y	Z
C	7.97391	-2.13163	0.5557
C	8.18004	-0.79369	0.22518
C	7.09427	0.0699	0.00905
C	5.76415	-0.44057	0.12684
C	5.56517	-1.81145	0.47113
C	6.68187	-2.63703	0.68002
C	7.27558	1.4552	-0.32522
C	4.64155	0.41595	-0.09429
C	4.86187	1.79054	-0.41426
C	6.209	2.27632	-0.5239
C	3.75137	2.62438	-0.60857
H	3.90898	3.67227	-0.84939
C	2.46079	2.12084	-0.51381
C	2.20982	0.7701	-0.22609
C	3.30845	-0.09839	0.00966
C	3.14836	-1.47677	0.39361
C	4.21959	-2.28931	0.60824
H	4.06658	-3.32452	0.9018
H	2.14624	-1.86601	0.52795
H	8.28921	1.83715	-0.4131
H	8.82654	-2.78394	0.72
H	9.19033	-0.40425	0.13266
H	6.52591	-3.67977	0.943
H	6.35885	3.32386	-0.77156
H	1.61586	2.77816	-0.69589
C	0.79463	0.31223	-0.18663
C	-0.14715	0.9925	0.60211
C	0.33889	-0.7672	-0.96528
C	-1.48731	0.6167	0.61755
H	0.18319	1.81364	1.23121
H	1.03898	-1.29808	-1.60283
C	-0.99755	-1.14657	-0.95443
H	-2.17588	1.14808	1.26382
C	-1.93666	-0.45656	-0.16806
H	-1.33929	-1.98179	-1.55543
C	-3.32677	-0.93896	-0.1701
N	-3.63861	-2.19914	-0.39123
N	-4.45193	-0.14798	0.0934
C	-5.01275	-2.2747	-0.2796
C	-5.55076	-1.00372	0.02418
C	-4.55124	1.27296	0.19969
C	-5.86509	-3.37761	-0.42526

C	-6.92225	-0.78527	0.16734
C	-5.08728	1.8416	1.35994
C	-4.14634	2.08878	-0.86185
H	-5.45575	-4.35592	-0.65467
C	-7.23147	-3.17151	-0.27346
C	-7.75175	-1.89369	0.01535
H	-7.3254	0.19816	0.38443
H	-5.39148	1.19635	2.1777
C	-5.21433	3.22781	1.45609
C	-4.26372	3.47345	-0.7516
H	-3.74334	1.63429	-1.76049
H	-7.9153	-4.00802	-0.38163
H	-8.82524	-1.76915	0.12158
H	-5.63085	3.66688	2.35753
C	-4.79946	4.04583	0.40405
H	-3.94454	4.10512	-1.57497
H	-4.89442	5.12444	0.48328

Table S5 Cartesian coordinates for the optimized structure **3c**.

Energy: -1777.34475091 hartrees

Atom	X	Y	Z
C	-7.8181	1.64958	-1.35795
C	-8.03797	0.54202	-0.54138
C	-6.96121	-0.18046	-0.00261
C	-5.62576	0.23718	-0.29585
C	-5.41295	1.36899	-1.1389
C	-6.52093	2.05906	-1.65737
C	-7.15762	-1.33164	0.83335
C	-4.51208	-0.47548	0.24751
C	-4.74824	-1.62206	1.06597
C	-6.09954	-2.02183	1.33937
C	-3.64672	-2.32325	1.57863
H	-3.81548	-3.20021	2.19748
C	-2.35199	-1.89582	1.32615
C	-2.08442	-0.75486	0.54843
C	-3.17415	-0.04583	-0.03087
C	-3.00011	1.07158	-0.91982
C	-4.06271	1.74417	-1.4424
H	-3.89822	2.57944	-2.11809
H	-1.99374	1.36529	-1.19125
H	-8.17519	-1.64482	1.05105
H	-8.66394	2.19478	-1.76631
H	-9.05218	0.22435	-0.31487
H	-6.35405	2.91925	-2.30007
H	-6.25995	-2.89491	1.9662
H	-1.5184	-2.43334	1.76693
C	-0.68595	-0.32932	0.37749
C	-0.13302	0.92756	0.51258
S	0.5607	-1.50712	0.02294
C	1.27449	0.95499	0.34429
H	-0.71899	1.80346	0.76441
C	1.81528	-0.28693	0.07841
H	1.86041	1.86029	0.42171
C	3.17477	-0.72281	-0.17924
N	3.45833	-1.95538	-0.55569
N	4.3141	0.08101	-0.08091
C	4.82667	-1.99501	-0.71882
C	5.39055	-0.73051	-0.42926
C	4.43349	1.43816	0.35375
C	5.6581	-3.0552	-1.10569
C	6.76157	-0.48242	-0.5038
C	4.61946	2.45315	-0.58945
C	4.39499	1.73907	1.71883

H	5.23265	-4.02759	-1.33053
C	7.02545	-2.81644	-1.18653
C	7.56904	-1.55015	-0.88926
H	7.1789	0.49223	-0.27341
H	4.64937	2.19954	-1.64416
C	4.75524	3.77488	-0.16334
C	4.52419	3.06322	2.13687
H	4.2593	0.93659	2.43641
H	7.69242	-3.62011	-1.48373
H	8.6424	-1.4028	-0.96188
H	4.89749	4.564	-0.89529
C	4.70406	4.08136	1.19785
H	4.48925	3.29837	3.19618
H	4.80656	5.11101	1.52675

Table S6 Cartesian coordinates for the optimized structure **3d**.

Energy: -1742.98956942 hartrees

Atom	X	Y	Z
N	1.16242	0.71439	0.00039
C	1.16764	2.11677	0.23528
C	2.25927	-0.0794	0.46223
C	1.84829	2.65164	1.34009
C	0.5235	2.99441	-0.65428
C	3.54875	0.06251	-0.10531
C	2.04358	-1.01193	1.48496
C	1.88496	4.03007	1.54456
H	2.34815	1.98565	2.03469
C	0.55115	4.36815	-0.42905
H	-0.00129	2.59654	-1.51587
C	4.61848	-0.73574	0.41026
C	3.82675	0.96338	-1.19039
C	3.07905	-1.79797	1.97336
H	1.04471	-1.10442	1.89922
C	1.23462	4.89807	0.6675
H	2.41854	4.42336	2.40522
H	0.04196	5.02829	-1.12525
C	5.93182	-0.60942	-0.13729
C	4.38014	-1.6739	1.46095
C	5.07957	1.07816	-1.71074
H	3.0136	1.5549	-1.59313
H	2.88835	-2.50789	2.77358
H	1.25913	5.97034	0.83461
C	6.17924	0.30724	-1.20342
C	7.00365	-1.40337	0.37619
C	5.47624	-2.4583	1.95605
H	5.26652	1.76309	-2.53353
C	7.47843	0.41693	-1.72496
C	8.28617	-1.25817	-0.17704
C	6.72961	-2.32773	1.4413
H	5.28148	-3.16449	2.75885
C	8.51826	-0.35717	-1.21437
H	7.66484	1.11527	-2.53635
H	9.10116	-1.86151	0.21369
H	7.5491	-2.92748	1.82816
H	9.5171	-0.25923	-1.62939
C	0.00962	0.04383	-0.48425
C	0.15986	-1.10387	-1.28321
C	-1.28251	0.48572	-0.17104
C	-0.96197	-1.77576	-1.75843
H	1.1551	-1.45503	-1.53276

C	-2.4123	-0.18849	-0.65745
H	-1.42992	1.36578	0.44234
C	-2.24811	-1.32808	-1.46076
H	-0.83089	-2.65077	-2.38822
H	-3.1076	-1.84562	-1.8684
C	-3.73236	0.37835	-0.32748
N	-3.92866	1.66888	-0.1592
N	-4.91235	-0.3643	-0.1964
C	-5.27758	1.81649	0.09791
C	-5.92077	0.5584	0.08083
C	-5.08506	-1.78054	-0.13691
C	-6.01884	2.97722	0.3566
C	-7.28511	0.41144	0.33854
C	-5.95522	-2.4066	-1.03558
C	-4.41439	-2.53272	0.83303
H	-5.52877	3.94521	0.36698
C	-7.38041	2.84151	0.6023
C	-8.00276	1.57688	0.59667
H	-7.76555	-0.56111	0.3415
H	-6.4626	-1.81139	-1.78783
C	-6.15168	-3.78602	-0.96168
C	-4.60515	-3.9123	0.89018
H	-3.74978	-2.03325	1.52963
H	-7.97926	3.72403	0.80646
H	-9.06742	1.50811	0.79914
H	-6.8282	-4.26949	-1.6599
C	-5.47498	-4.54155	-0.00295
H	-4.07971	-4.49488	1.64073
H	-5.62525	-5.61553	0.04912

Table S7 Cartesian coordinates for the optimized structure **3e**.

Energy: -1742.99108680 hartrees

Atom	X	Y	Z
N	-1.38856	0.94583	-0.46236
C	-1.63828	2.34442	-0.53018
C	-2.4436	0.03097	-0.77774
C	-2.58025	2.85985	-1.43348
C	-0.97052	3.2299	0.33388
C	-3.59348	-0.06135	0.04333
C	-2.32595	-0.77991	-1.91392
C	-2.84704	4.22781	-1.46734
H	-3.1012	2.18578	-2.10439
C	-1.23252	4.5964	0.27958
H	-0.24974	2.83975	1.04456
C	-4.63681	-0.96427	-0.33594
C	-3.75368	0.70127	1.25122
C	-3.33054	-1.67	-2.26926
H	-1.4305	-0.69636	-2.52116
C	-2.17407	5.10604	-0.61771
H	-3.58075	4.6073	-2.17274
H	-0.70642	5.26492	0.95519
C	-5.81515	-1.07108	0.46463
C	-4.50303	-1.77514	-1.50438
C	-4.8773	0.59379	2.01242
H	-2.95578	1.36896	1.55239
H	-3.21899	-2.28345	-3.15898
H	-2.3813	6.17105	-0.65096
C	-5.95251	-0.28455	1.64801
C	-6.86098	-1.96916	0.08726
C	-5.56886	-2.67017	-1.85708
H	-4.97498	1.17755	2.92392
C	-7.12092	-0.40258	2.41789
C	-8.01139	-2.05209	0.88838
C	-6.69654	-2.76094	-1.1001
H	-5.45458	-3.27859	-2.75026
C	-8.13794	-1.27603	2.03872
H	-7.22322	0.19709	3.31828
H	-8.80668	-2.73453	0.60083
H	-7.49533	-3.44183	-1.38152
H	-9.03507	-1.35493	2.64567
C	-0.07264	0.43844	-0.33877
C	0.14552	-0.79935	0.2946
C	1.03723	1.12711	-0.85714
C	1.42548	-1.32083	0.4067
H	-0.69862	-1.34633	0.70024

C	2.31997	0.60638	-0.72773
H	0.89176	2.0673	-1.37663
C	2.54281	-0.62466	-0.08927
H	1.58476	-2.27944	0.88769
H	3.14751	1.15319	-1.16425
C	3.86272	-1.25819	0.02945
N	4.02284	-2.56535	0.06893
N	5.0827	-0.56998	0.07554
C	5.38463	-2.77903	0.14801
C	6.07594	-1.54643	0.15272
C	5.32361	0.82776	0.23951
C	6.10115	-3.98113	0.219
C	7.46598	-1.46726	0.25035
C	6.09033	1.51159	-0.71004
C	4.82734	1.50194	1.3602
H	5.57485	-4.93	0.21125
C	7.48739	-3.91228	0.30458
C	8.15906	-2.67372	0.32335
H	7.98468	-0.51468	0.27118
H	6.46496	0.97686	-1.57686
C	6.35612	2.87045	-0.53712
C	5.08547	2.86271	1.51777
H	4.24485	0.9569	2.09518
H	8.06723	-4.82869	0.36113
H	9.24235	-2.65766	0.39707
H	6.95179	3.39869	-1.27541
C	5.85136	3.54917	0.57305
H	4.69561	3.38479	2.38631
H	6.05514	4.60765	0.70282

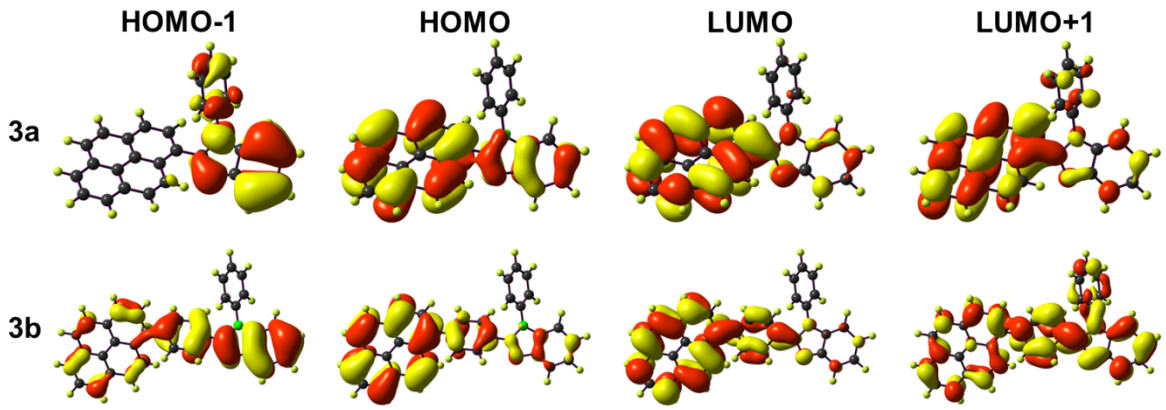

Fig. S11 Frontier molecular orbitals of the selected compounds **3a** & **3b**.

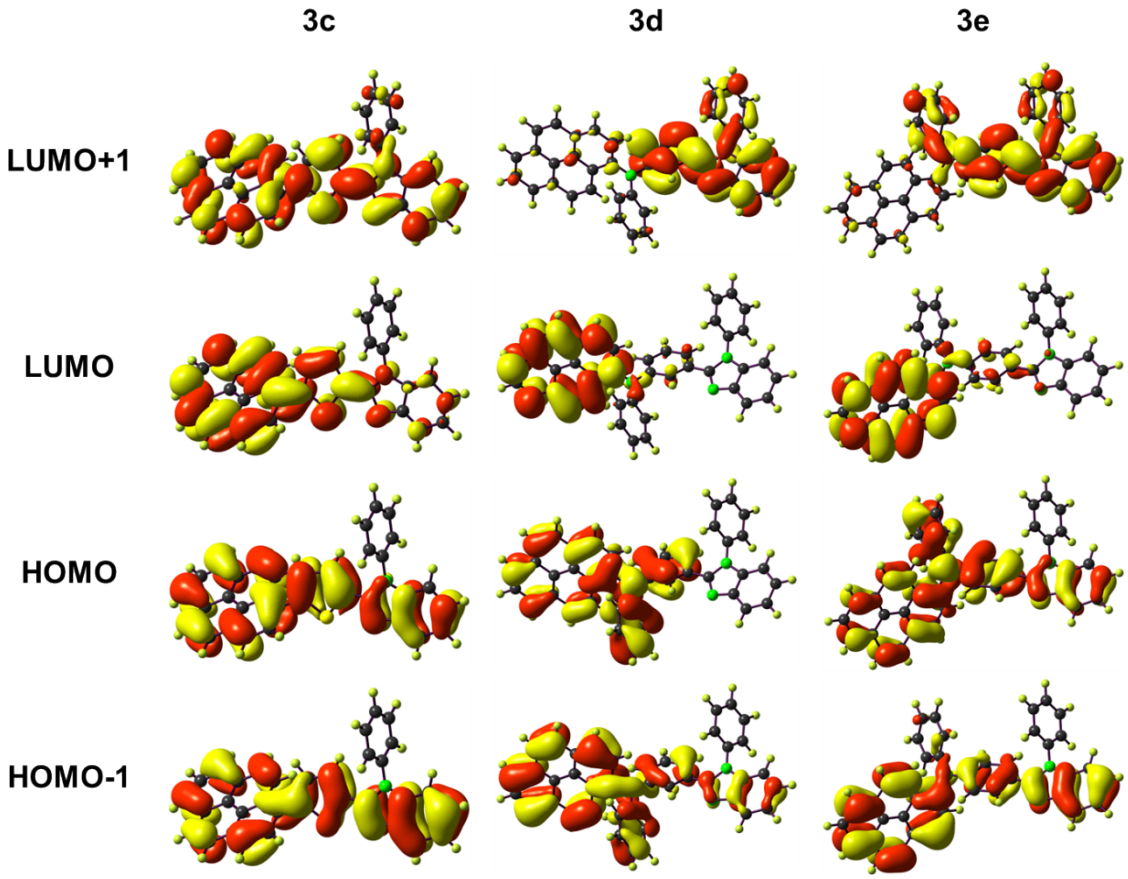

Fig. S12 Frontier molecular orbitals of the selected compounds **3c** – **3e**.

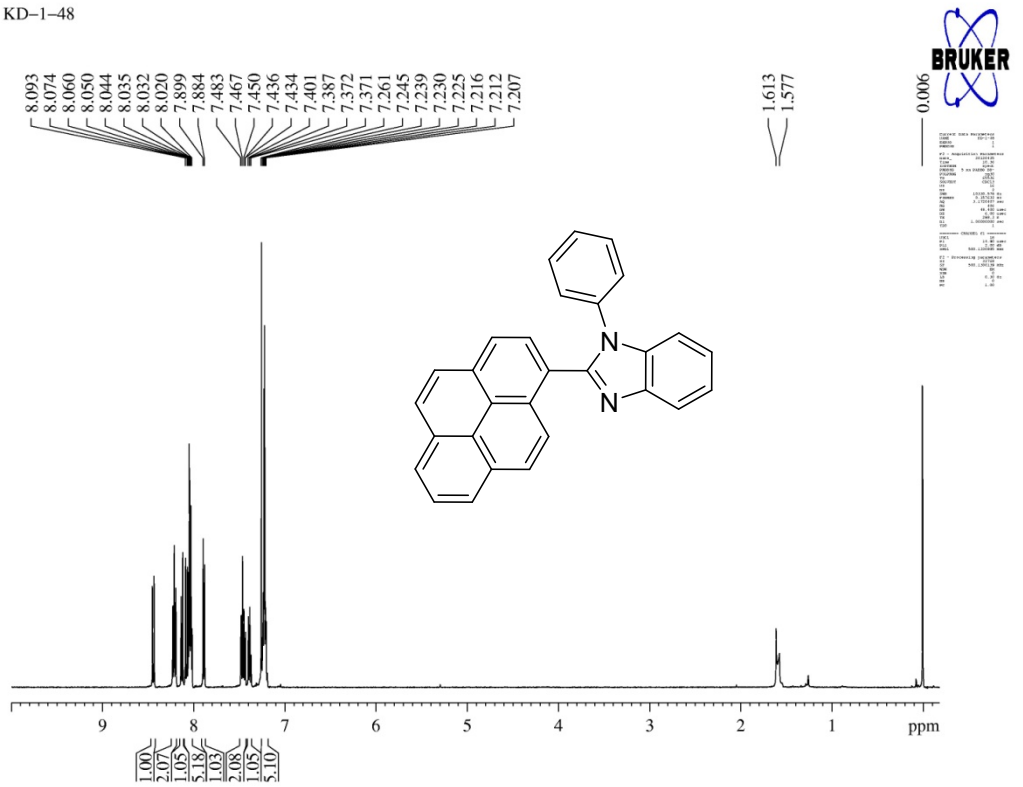

Fig. S13 ^{1}H NMR spectrum of **3a** in $CDCl_3$.

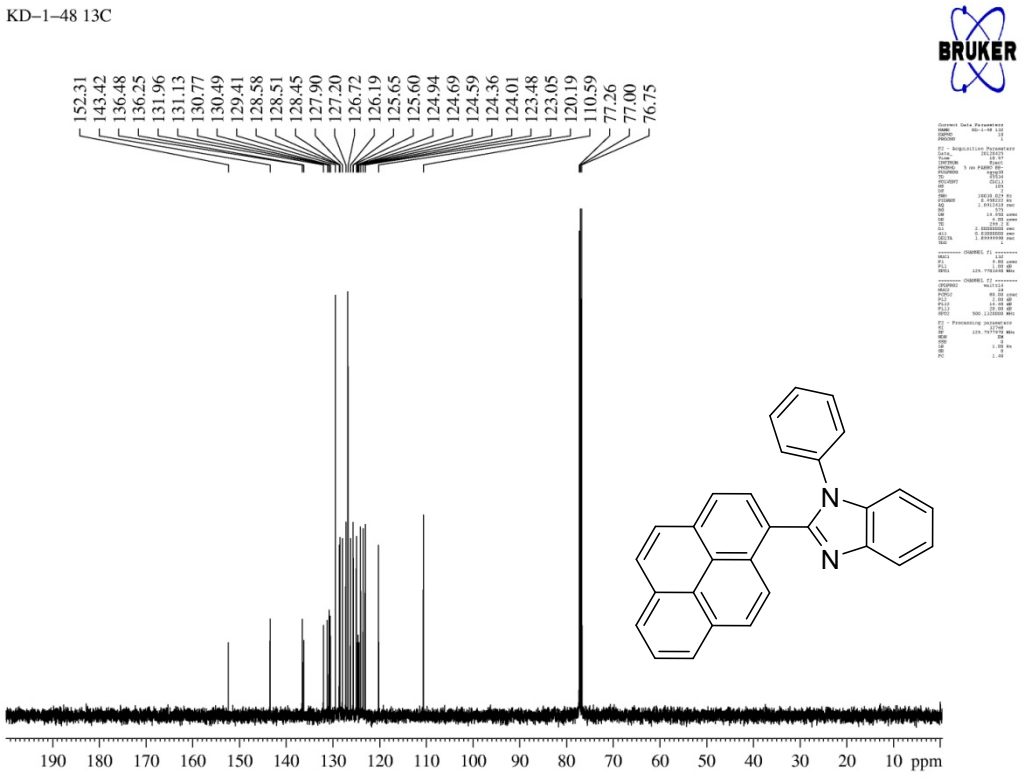

Fig. S14 ^{13}C NMR spectrum of **3a** in $CDCl_3$.

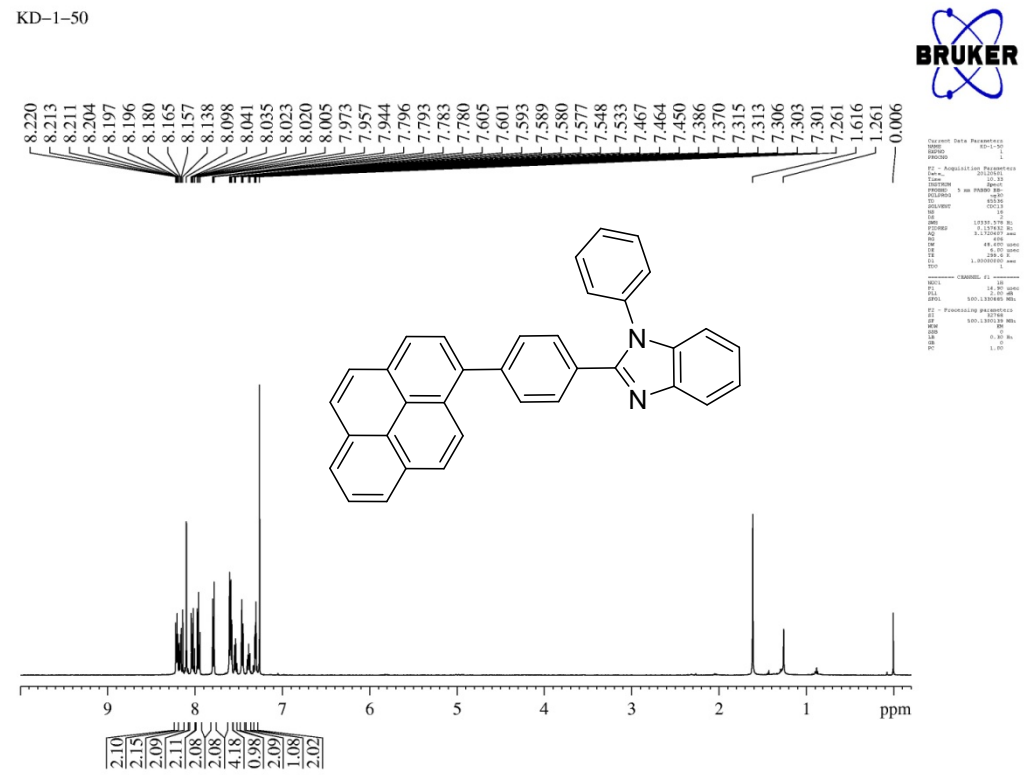

Fig. S15 ^{1}H NMR spectrum of **3b** in $CDCl_3$.

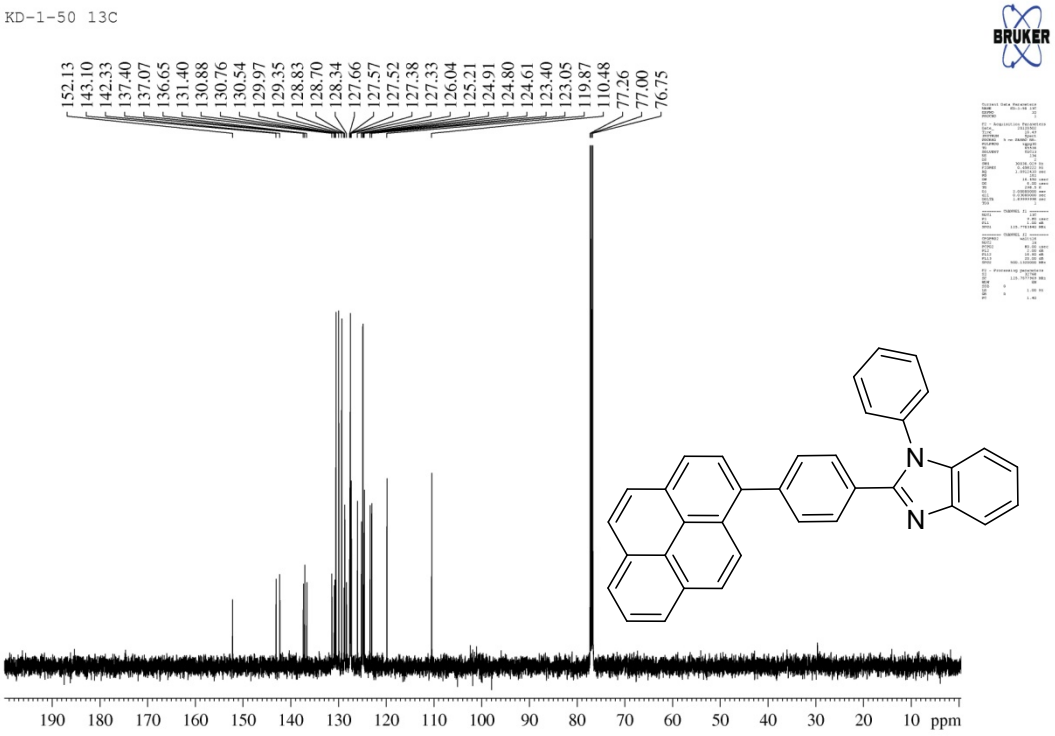

Fig. S16 ^{13}C NMR spectrum of **3b** in $CDCl_3$.

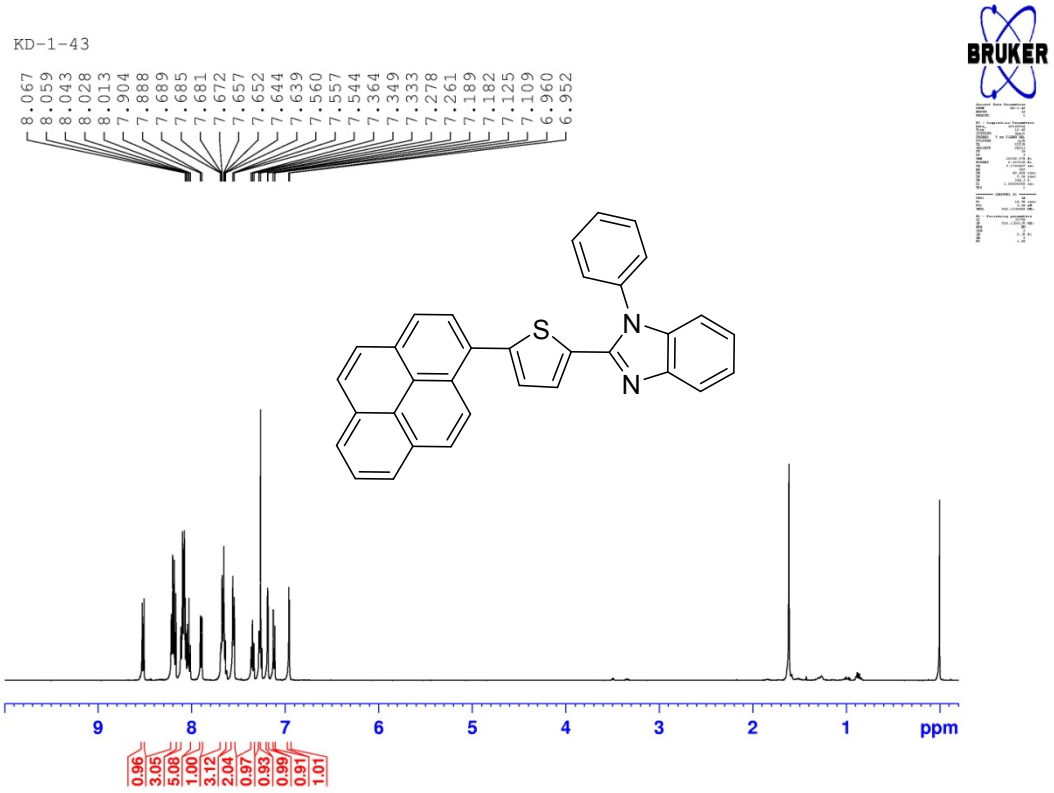

Fig. S17 ^{1}H NMR spectrum of **3c** in $CDCl_3$.

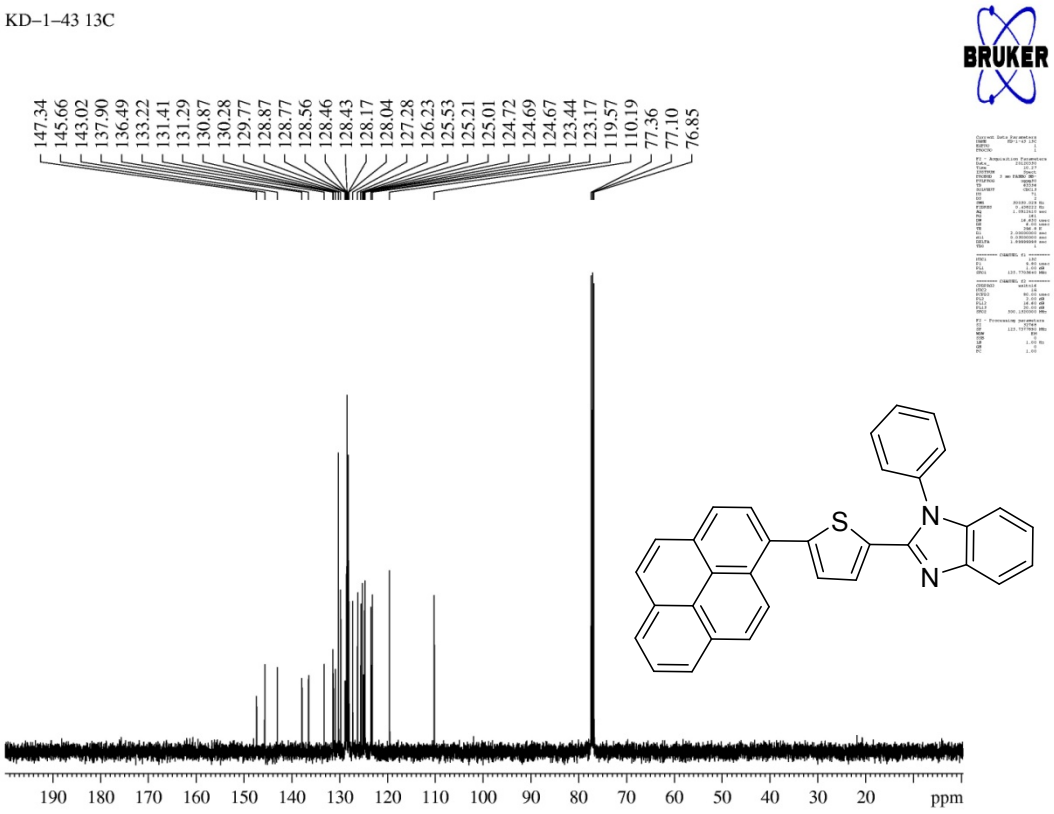

Fig. S18 ^{13}C NMR spectrum of **3c** in $CDCl_3$.

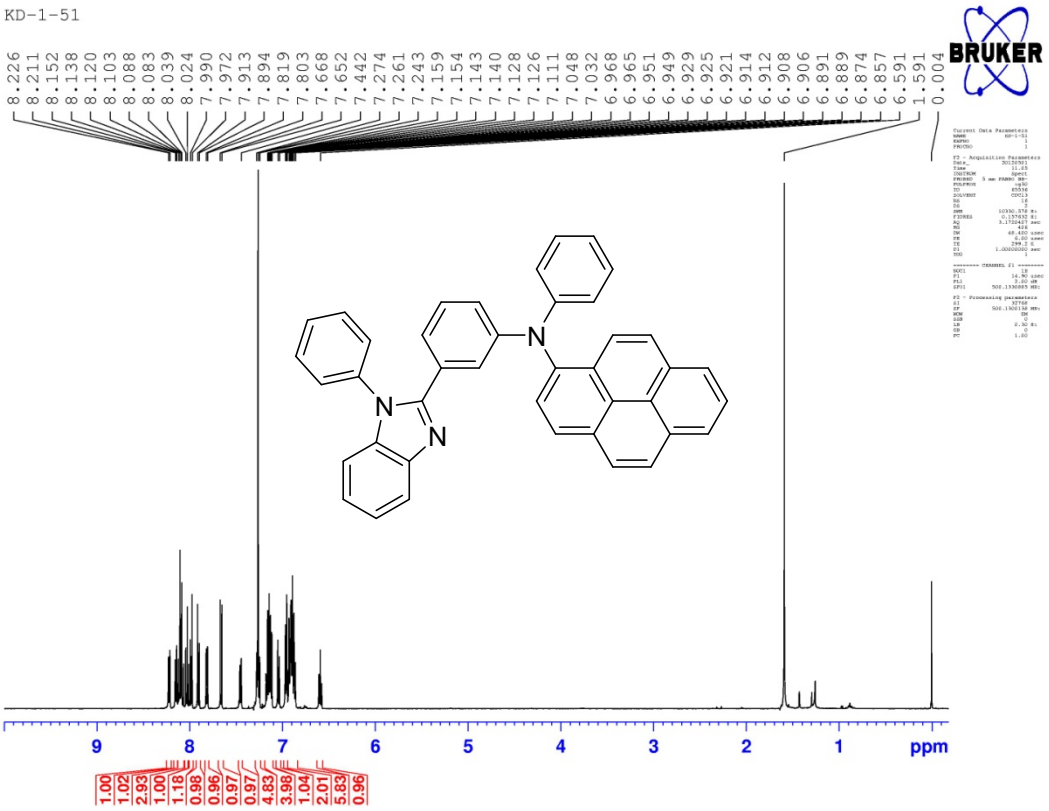

Fig. S19 ^{1}H NMR spectrum of **3d** in $CDCl_3$.

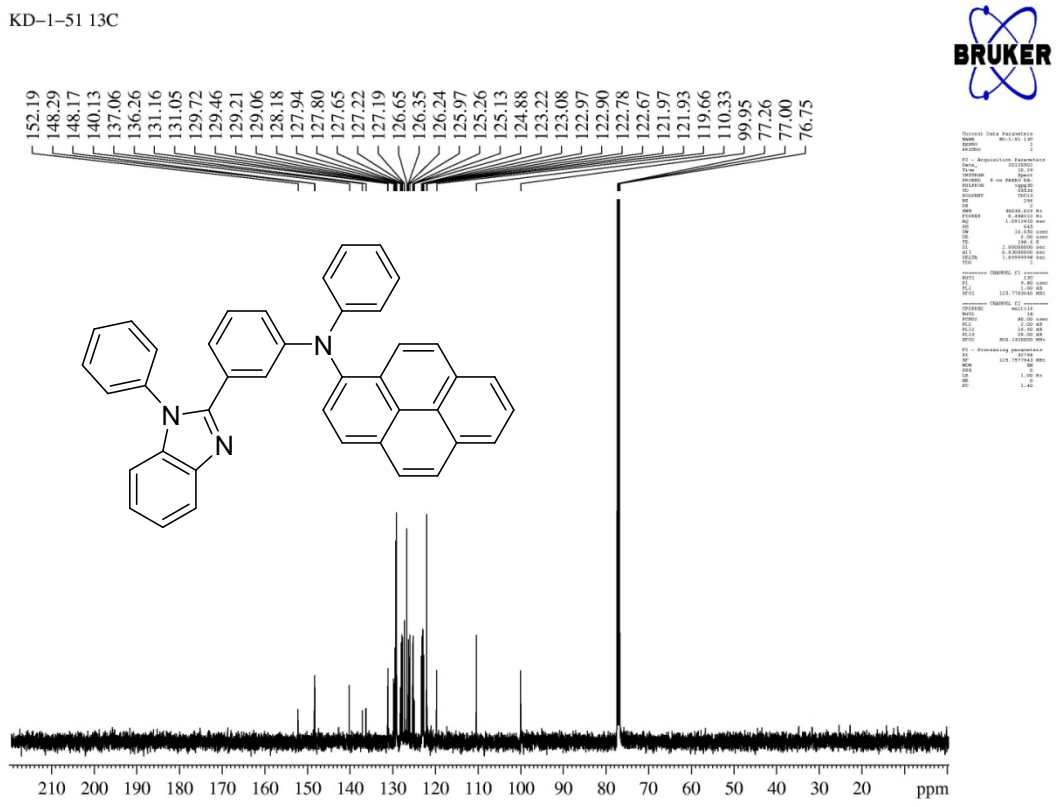

Fig. S20 ^{13}C NMR spectrum of **3d** in $CDCl_3$.

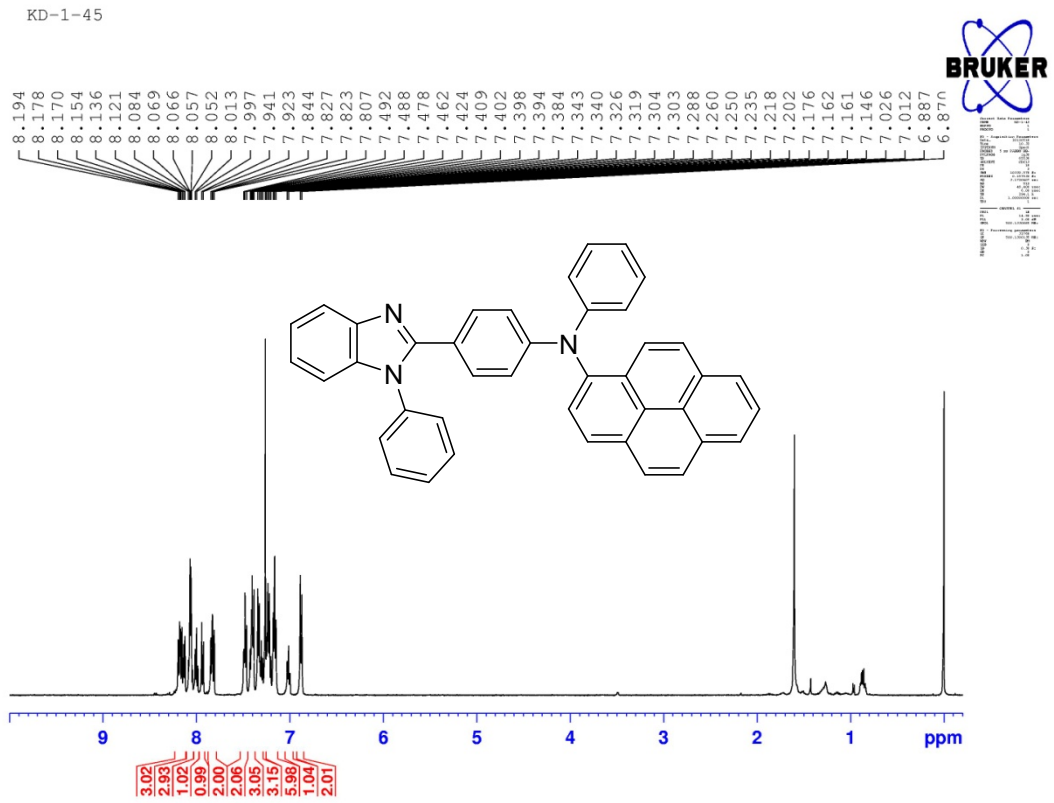

Fig. S21 ^{1}H NMR spectrum of **3e** in $CDCl_3$.

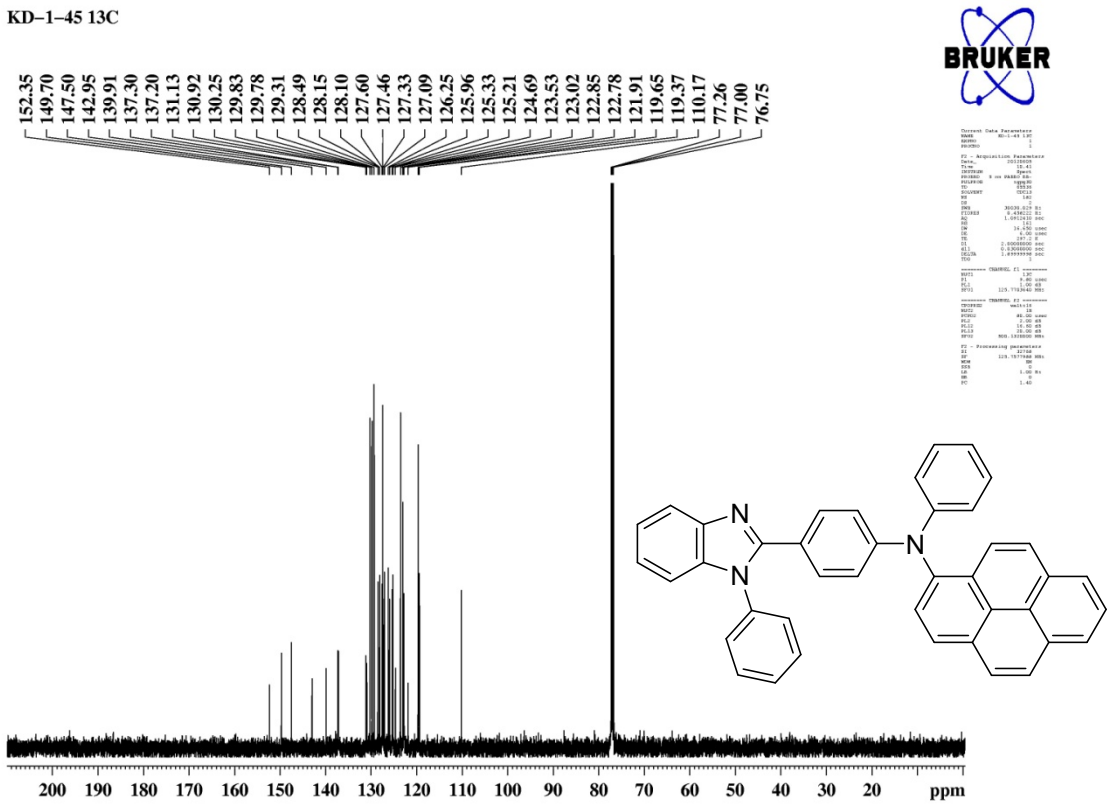

Fig. S22 ^{13}C NMR spectrum of **3e** in $CDCl_3$.