Supporting Information

Hexaethylsubporphyrins: β-alkyl analogues in subporphyrin family

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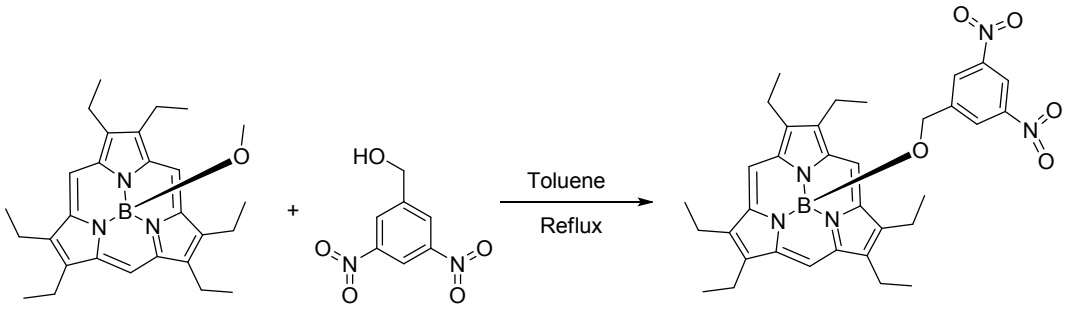
Instrumentation and materials

Crystallographic data for **4** and **5.DN** collected on Oxford Gemini A Ultra diffractometer with dual source. Cu-Kα (λ = 1.54184 Å) radiation was used to collect the X-ray reflections of the crystal. Data reduction was performed using CrysAlisPro 171.33.55 software.[S1] Structures were solved and refined using SHELXL-97[S2] with anisotropic displacement parameters for non-H atoms. Hydrogen atoms on O and N were experimentally located in difference electron density maps. All C−H atoms were fixed geometrically using HFIX command in SHELX-TL with anisotropic displacement parameters for non-H atoms. All H atoms of **4** and **5.DN** were fixed geometrically. Empirical absorption correction was done using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. A check of the final CIF file using PLATON[S3] did not show any missed symmetry. In case of **5.DN** some solvent accessible voids were observed. The contribution to the scattering factors from this was removed by SQUEEZE[S4] in PLATON. PLATON was used as incorporated in WinGX.[S5] Crystallographic data (excluding the structure factor) for the structure **4** and **5.DN** in this paper has been deposited in the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 1414845-1414846. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk) or via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of 3,5-dinitrobenzylalcoxo-2,3,7,8,12,13-hexaethyl(subporphyrinato)boron(III) (5.DN).



5 (9.0 mg, 0.02 mmol) and 3,5-dinitrobenzylalcohol (4.9 mg, 0.024 mmol) were taken in R.B. and dissolved in toluene (5.0 mL) and the reaction mixture was heated to reflux for 30 min. Reaction mixture was cooled and solvent was evaporated. Crude was passed through a thin silica gel column pad and the **5.DN** was obtained as a yellow powder in quantitative yield by eluting with EtOAc/hexane (10%). Single crystal for X-ray diffraction analysis was grown from slow diffusion of hexane in to ether solution of **5.DN**.

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.64 (br, 1H, -Ar*CH*), 8.62 (s, 3H, -*meso*), 7.16 (br, 2H, -Ar-*CH*), 3.30 (m, 12H, -CH_3*CH_2*), 2.00 (br, 2H, -O*CH_2*), 1.50 (m, 18H, -*CH_3*CH_2).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 147.4, 142.2, 133.8, 126.3, 125.1, 116.1, 98.3, 65.8, 18.7, 17.4.

^{11}B NMR (160 MHz, $CDCl_3$) δ (ppm) -15.3.

HR-ESI-MS (positive mode) *m/z* = 410.2764 (calcd. for $C_{27}H_{33}BN_3$ = 410.2768 [M-**DN**]$^{+}$).

UV-Vis (in CH_2Cl_2) λ [nm] (ε [$M^{-1}cm^{-1}$]) 324 (12258), 339 (23623), 437 (1879), 463 (4151).

Fluorescence (in CH_2Cl_2, λ_{ex} = 350 nm) λ_{max} [nm] 467, 482, 499.

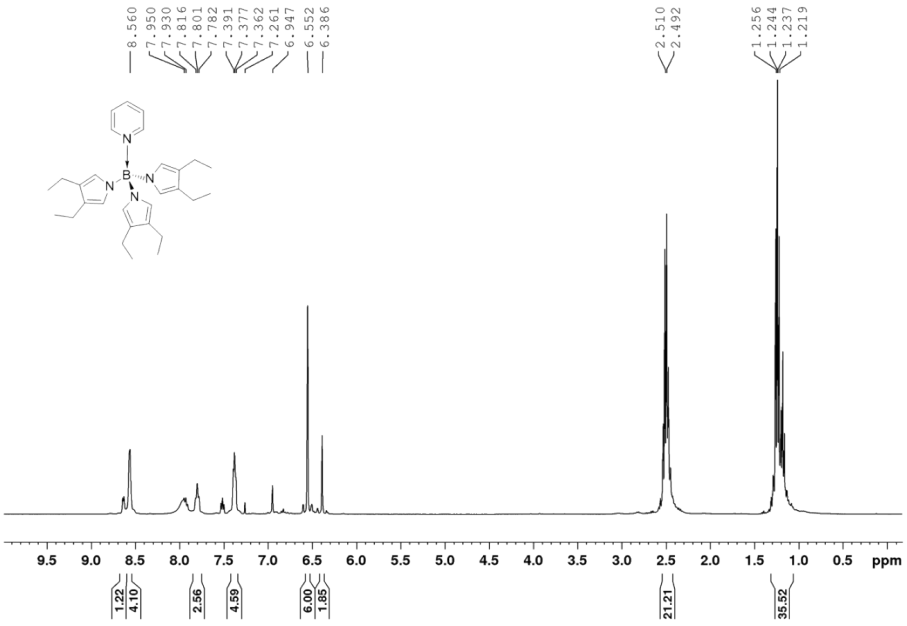


Figure S1: ^{1}H NMR spectrum of **6** in $CDCl_3$.

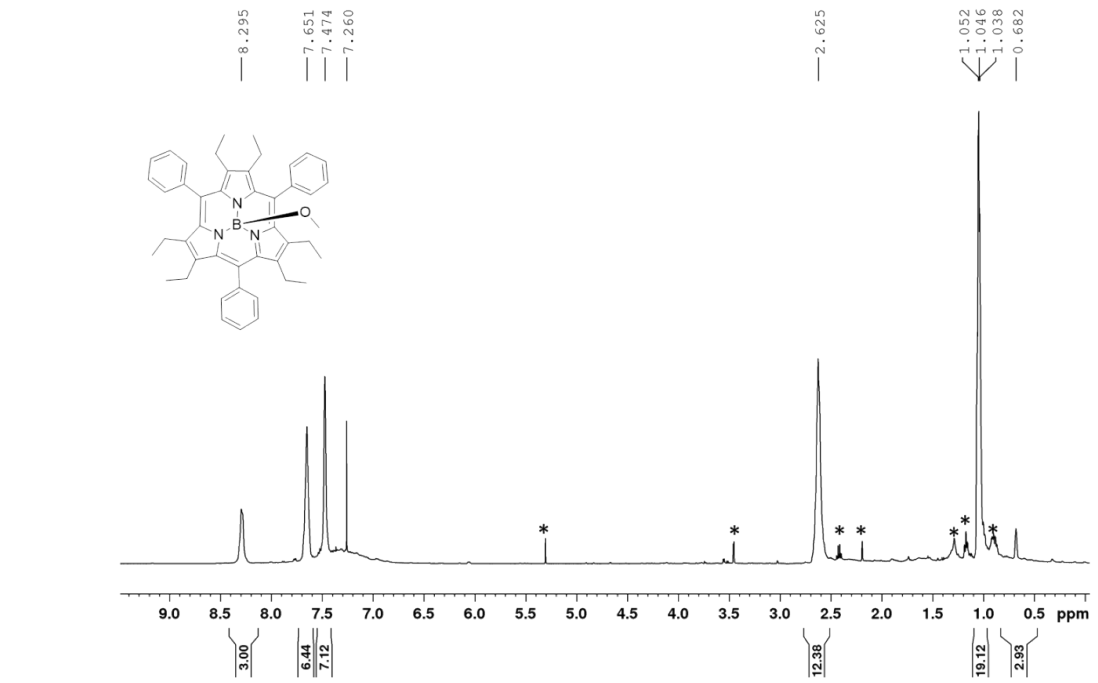


Figure S2: ^{1}H NMR spectrum of **4** in $CDCl_3$.

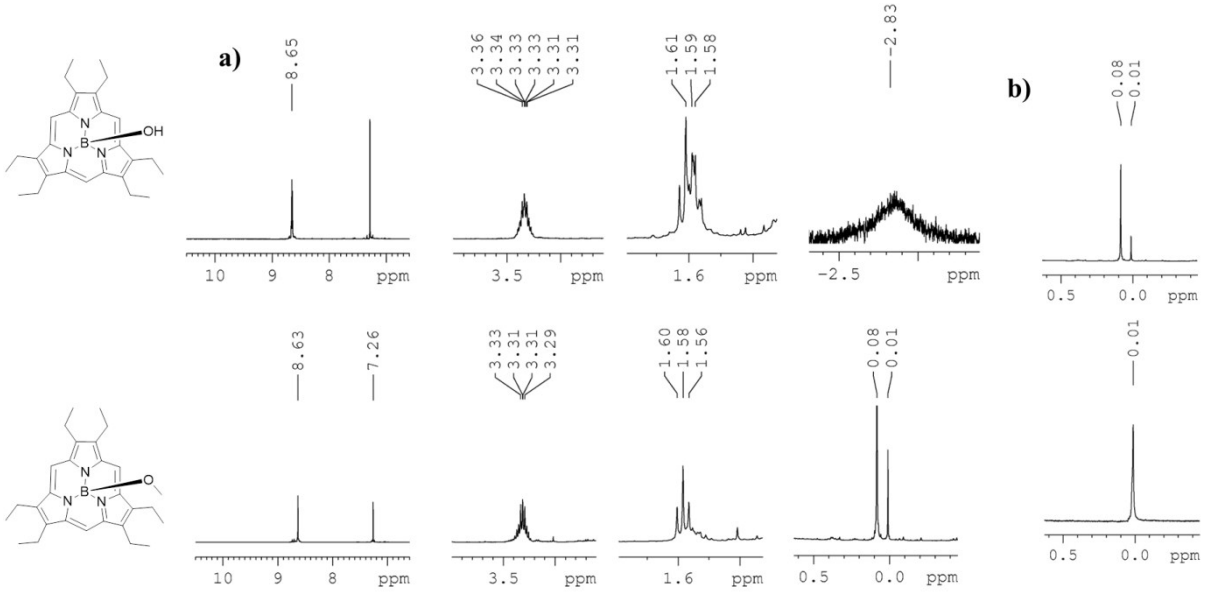


Figure S3: (a) ^{1}H NMR spectrum of **5** in $CDCl_3$. (b) MeOH-d_4-exchang of B-OMe.

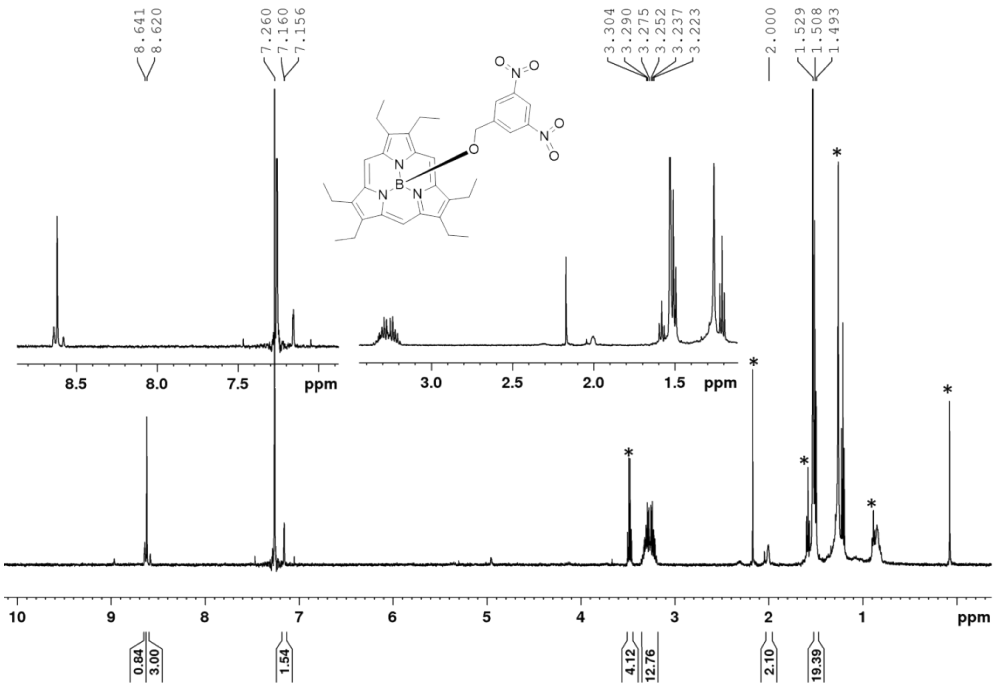


Figure S4: ^{1}H NMR spectrum of **5.DN** in $CDCl_3$.

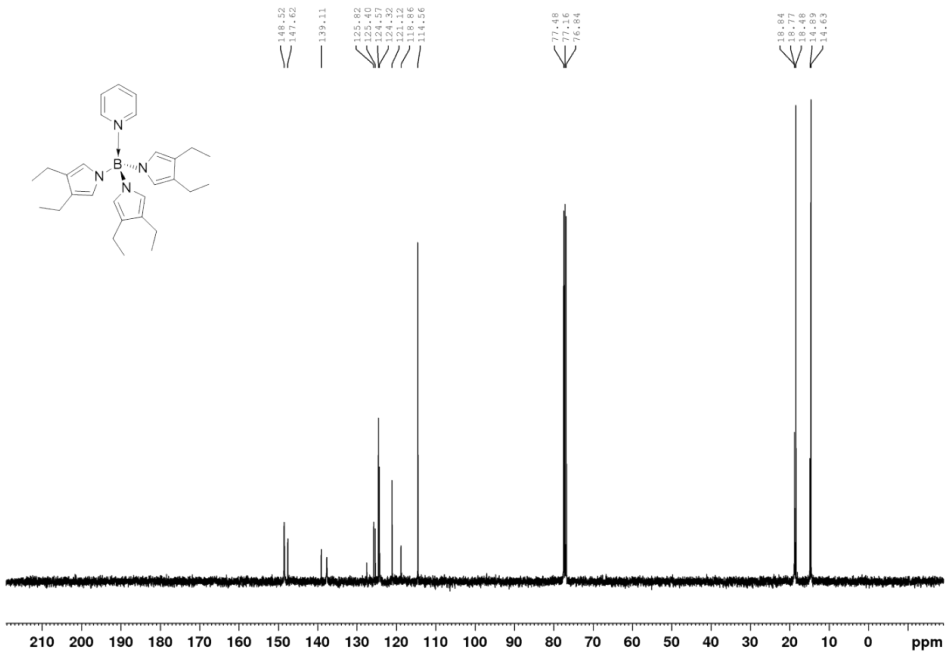


Figure S5: ^{13}C NMR spectrum of **6** in $CDCl_3$.

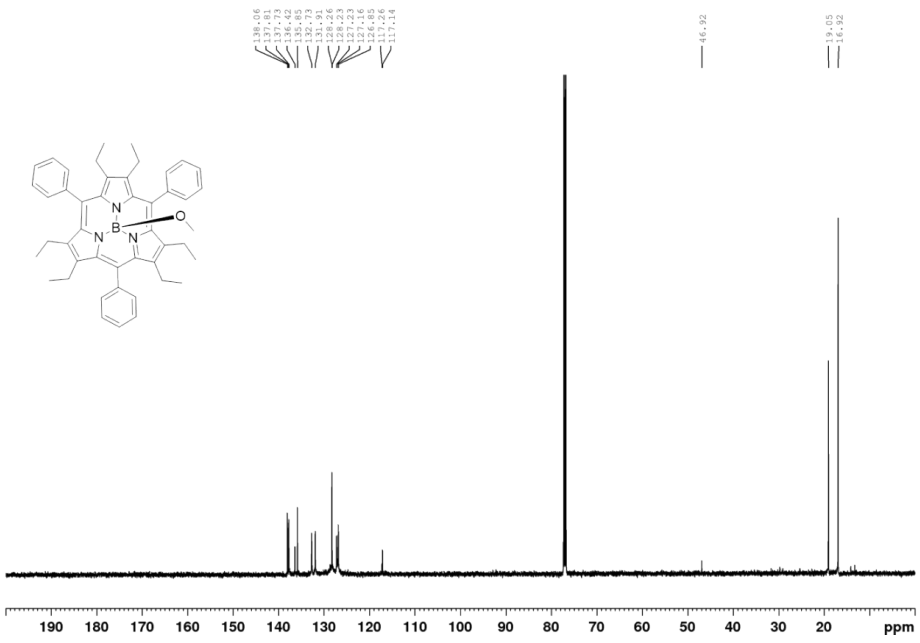


Figure S6: ^{13}C NMR spectrum of **4** in $CDCl_3$.

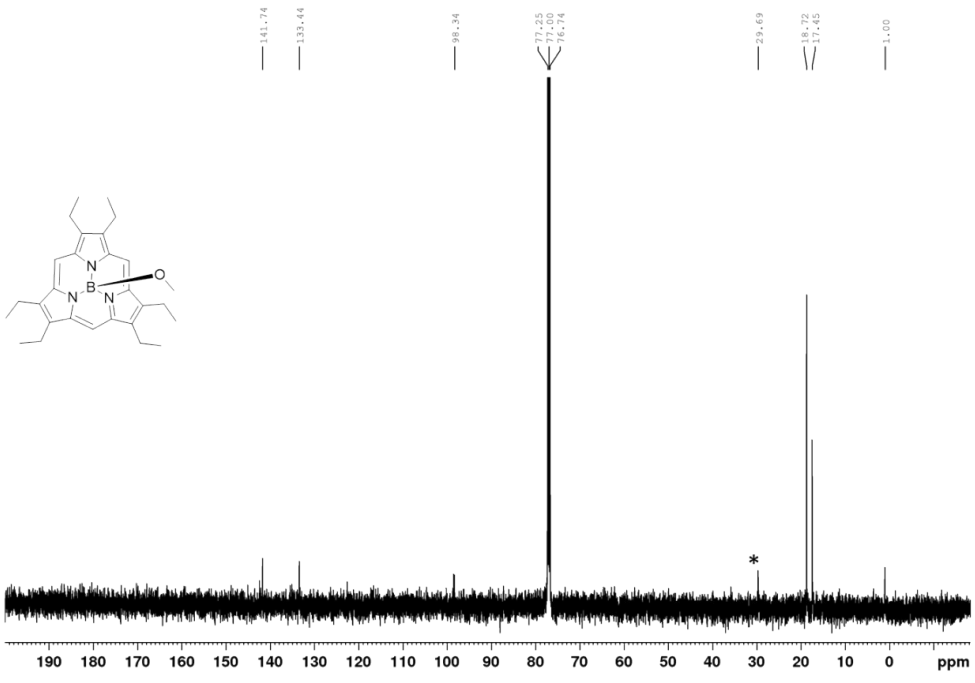


Figure S7: ^{13}C NMR spectrum of **5** in $CDCl_3$.

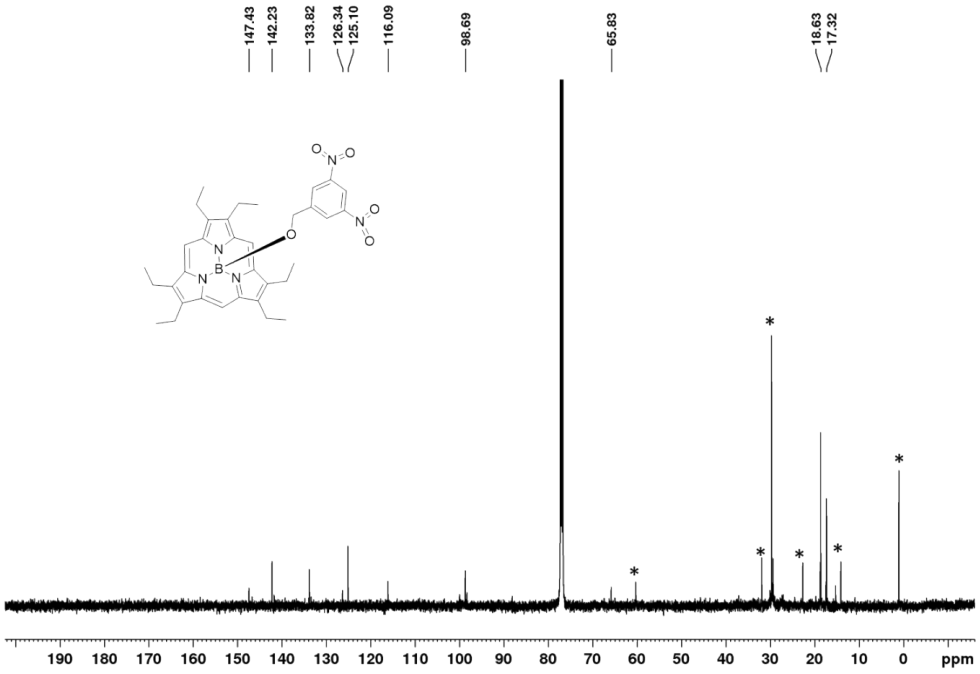


Figure S8: ^{13}C NMR spectrum of **5.DN** in $CDCl_3$.

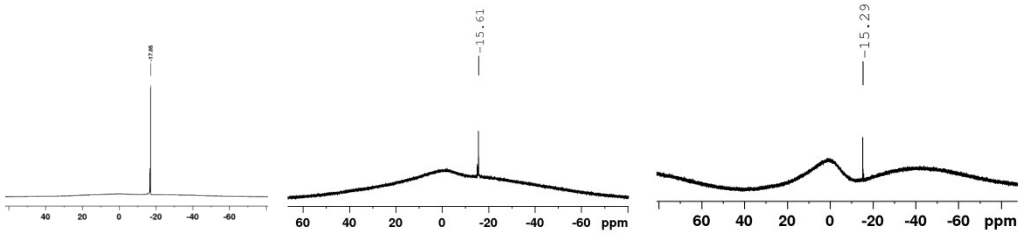


Figure S9: ^{11}B NMR spectra of **4** (left) and **5** (middle) and **5.DN** (right) in $CDCl_3$.

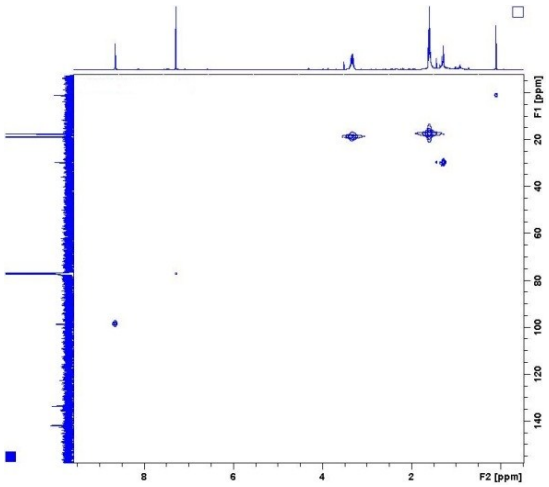


Figure S10: HMQC NMR spectrum of **5** in $CDCl_3$.

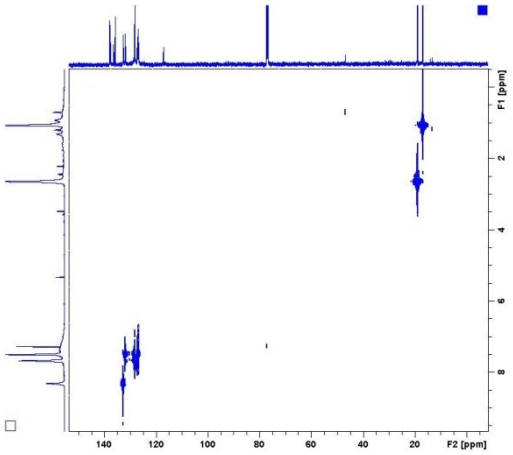


Figure S11: ^{1}H-^{13}C COSY NMR spectra of **4** in $CDCl_3$.

IUCR check CIF Alerts:

Alert level A
PLAT026_ALERT_3_A Ratio Observed / Unique Reflections too Low .... 16 %

Alert level B
RFACR01_ALERT_3_B The value of the weighted R factor is > 0.35
Weighted R factor given 0.392
PLAT084_ALERT_3_B High wR2 Value (i.e. > 0.25) ..... 0.39 Report
PLAT230_ALERT_2_B Hirshfeld Test Diff for N1 -- B1 .. 7.8 su
PLAT230_ALERT_2_B Hirshfeld Test Diff for N4 -- C31 .. 7.3 su
PLAT340_ALERT_3_B Low Bond Precision on C-C Bonds ..... 0.0159 Ang.

PLAT782_ALERT_2_B Unusual Bond Geometry for C-NO2 Moiety Around N4 Check
PLAT782_ALERT_2_B Unusual Bond Geometry for C-NO2 Moiety Around N5 Check

Author response: After several attempts of crystallization the obtained crystal was the best. Its quality was not good and it was weakly diffracting, hence we failed to get good diffraction data even after long run of data collection. We have done the structure refinement in **SHELXL-97,** with some constraints which gave finally the best solution so far achieved.

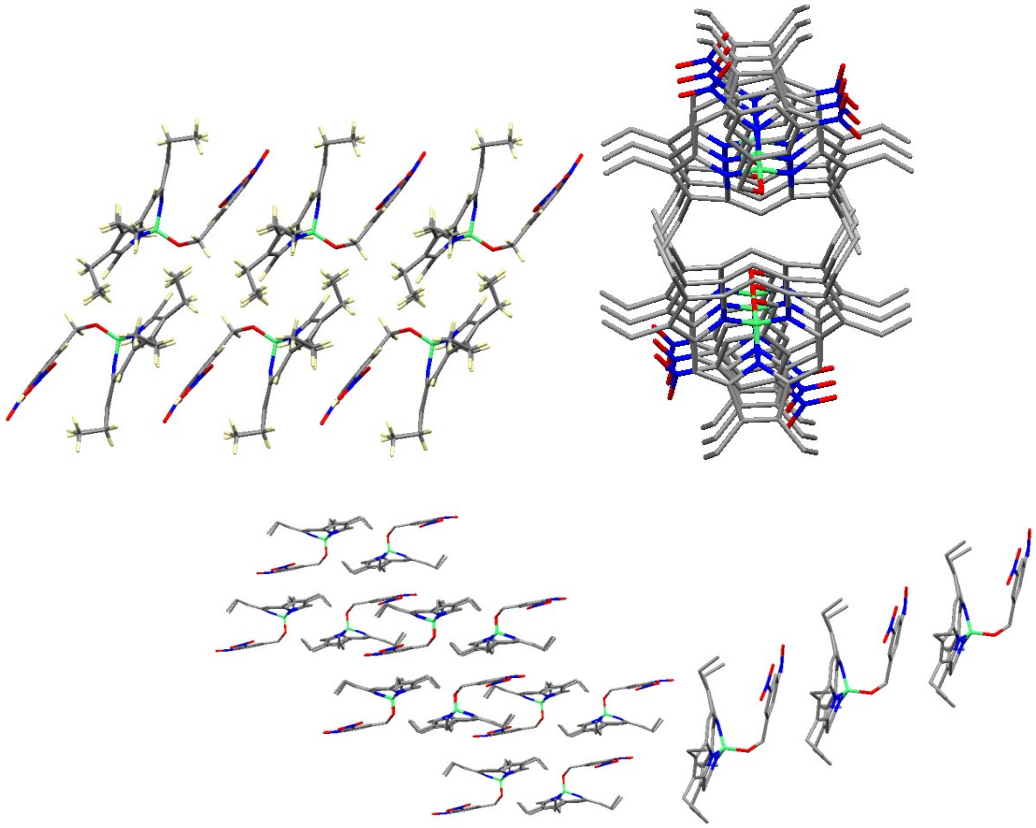


Figure S12: Crystal packing diagram of **5.DN**.

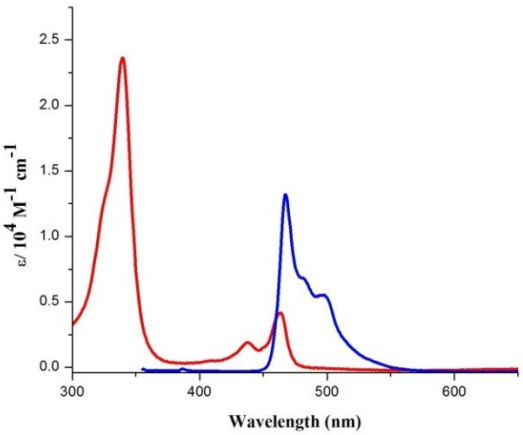
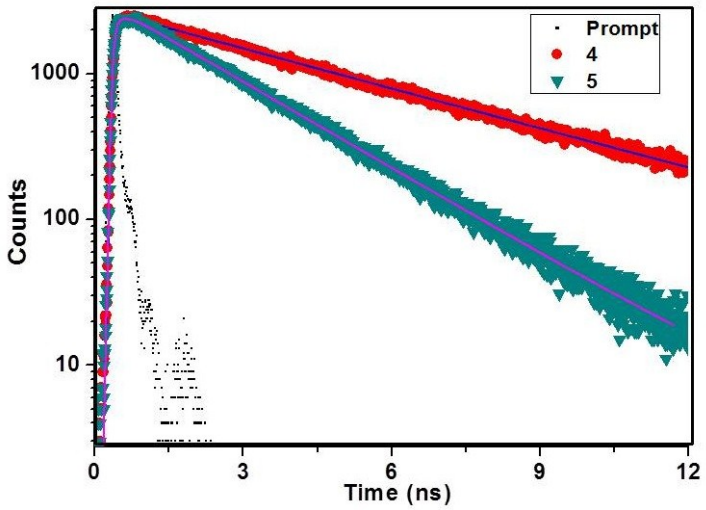


Figure S13: Uv-vis (red) and fluorescence (blue) spectra of **5.DN** in CH_2Cl_2.



Sample	$\lambda_{emission}$ (nm)	τ_{dacay} (a1)	χ^2
4	465	4.68 ns (100%)	1.17
5	460	2.19 ns (100%)	1.06

Figure S14: Fluorescence decay plot for **4** (red) and **5** (cyan) with prompt (black). Table summarizes the life average S_1 life time calculated from TCSPC.

DFT calculations:[S6]

Table S1: Transition, harmonic oscillator strength and symmetry calculated (H = HOMO, L = LUMO) from DFT for **4.**

Wavelength (nm)	Osc. Strength	Symmetry	Major contribs
427.3961069	0.001	Singlet-A	H-1->LUMO (51%), HOMO->L+1 (48%)
426.8075894	0.0007	Singlet-A	H-1->L+1 (46%), HOMO->LUMO (52%)
353.8539204	0.0223	Singlet-A	H-2->LUMO (29%), H-2->L+1 (61%)
348.1211193	0.0028	Singlet-A	H-2->LUMO (60%), H-2->L+1 (31%)
342.4008192	0.1645	Singlet-A	H-3->LUMO (68%), H-1->L+1 (11%)
336.0346288	0.6472	Singlet-A	H-3->L+1 (10%), H-1->LUMO (19%), H-1->L+1 (20%), HOMO->LUMO (16%), HOMO->L+1 (19%)
330.3755506	0.532	Singlet-A	H-3->LUMO (14%), H-3->L+1 (12%), H-1->LUMO (17%), H-1->L+1 (10%), HOMO->L+1 (23%)
324.054722	0.1744	Singlet-A	H-3->LUMO (11%), H-3->L+1 (66%)
311.8528476	0.0335	Singlet-A	H-4->LUMO (50%), H-4->L+1 (45%)
305.1446842	0.0248	Singlet-A	H-4->LUMO (43%), H-4->L+1 (49%)
297.7505683	0.2537	Singlet-A	H-5->LUMO (87%)
294.9877151	0.2342	Singlet-A	H-5->L+1 (87%)
288.4272476	0.001	Singlet-A	HOMO->L+2 (21%), HOMO->L+3 (68%)
286.2893681	0.0035	Singlet-A	HOMO->L+2 (45%), HOMO->L+3 (16%), HOMO->L+5 (18%)
284.8816356	0.0203	Singlet-A	HOMO->L+2 (20%), HOMO->L+4 (27%), HOMO->L+5 (25%)
284.2415843	0.0105	Singlet-A	H-1->L+2 (35%), H-1->L+3 (45%)
283.5136097	0.0081	Singlet-A	HOMO->L+4 (46%), HOMO->L+5 (23%)
282.8087058	0.003	Singlet-A	H-1->L+2 (46%), H-1->L+3 (38%)
281.3327357	0.0058	Singlet-A	H-1->L+4 (66%), H-1->L+5 (14%)
280.7975192	0.0011	Singlet-A	H-1->L+6 (14%), HOMO->L+5 (26%), HOMO->L+6 (42%)

Table S2: Transition, harmonic oscillator strength and symmetry calculated (H = HOMO, L = LUMO) from DFT for **5.**

Wavelength (nm)	Osc. Strength	Symmetry	Major contribs
419.344303	0.0288	Singlet-A	H-1->L+1 (35%), HOMO->LUMO (61%)
418.8626238	0.0258	Singlet-A	H-1->LUMO (37%), HOMO->L+1 (59%)
336.0255214	0.0208	Singlet-A	H-2->LUMO (87%)
329.0952292	0.0857	Singlet-A	H-3->LUMO (32%), H-2->L+1 (46%)
326.8396073	0.0591	Singlet-A	H-3->L+1 (81%)
321.4335182	0.2411	Singlet-A	H-2->L+1 (40%), H-1->LUMO (24%), HOMO->L+1 (13%)
317.0442813	0.5093	Singlet-A	H-1->L+1 (47%), HOMO->LUMO (24%)
312.3556714	0.3017	Singlet-A	H-3->LUMO (53%), H-1->LUMO (22%), HOMO->L+1 (12%)
307.4602273	0.0255	Singlet-A	H-4->LUMO (92%)
299.3176009	0.0338	Singlet-A	H-4->L+1 (88%)
287.3576615	0.2026	Singlet-A	H-5->LUMO (91%)
285.7680741	0.2163	Singlet-A	H-5->L+1 (90%)
239.8733466	0.0026	Singlet-A	H-6->LUMO (98%)
238.6773508	0.0048	Singlet-A	H-6->L+1 (98%)
227.4631454	0.0001	Singlet-A	H-8->LUMO (24%), H-8->L+1 (23%), H-7->LUMO (27%), H-7->L+1 (24%)
220.7405356	0.0014	Singlet-A	H-8->LUMO (31%), H-8->L+1 (14%), H-7->LUMO (33%), H-7->L+1 (17%)
218.3920252	0.0024	Singlet-A	H-8->L+1 (29%), H-7->LUMO (16%), HOMO->L+2 (46%)
217.5986111	0.0053	Singlet-A	H-8->LUMO (19%), H-7->L+1 (35%), HOMO->L+3 (33%)
212.0932252	0.0247	Singlet-A	H-1->L+2 (17%), H-1->L+3 (34%), HOMO->L+2 (23%)
211.9880598	0.0349	Singlet-A	H-1->L+2 (46%), H-1->L+3 (12%), HOMO->L+3 (22%)

Coordinates of the optimized structure **5**:

Tag	Symbol	X	Y	Z
1	N	0.014161	1.350516	0.733769
2	N	1.225477	-0.703688	0.464859
3	N	-1.178523	-0.708218	0.441754
4	O	0.104002	-0.356784	2.565101
5	C	-0.671268	3.426085	0.155624
6	C	1.148585	2.074416	0.495222
7	C	1.257773	-1.955744	-0.075787
8	C	0.038886	-2.638849	-0.283122
9	C	2.373722	1.389109	0.33342
10	C	2.381455	-0.019727	0.225352
11	C	-2.325997	-0.027287	0.144796
12	C	-1.188061	-1.9622	-0.103494
13	C	0.720938	3.427595	0.188373
14	C	-1.108861	2.071686	0.442234
15	C	-2.325516	1.382808	0.236897
16	C	3.302865	-0.965903	-0.379605
17	C	2.609876	-2.159118	-0.566043
18	C	-3.221375	-0.977604	-0.490603
19	C	4.719171	-0.645716	-0.767302
20	H	4.756968	0.362924	-1.1991
21	H	5.048685	-1.326426	-1.560501
22	C	-1.589922	4.564369	-0.196993
23	H	-1.110526	5.513123	0.071328
24	H	-2.495566	4.499891	0.419316
25	C	-2.519428	-2.170134	-0.644341
26	C	-4.621542	-0.661466	-0.936289
27	H	-4.917939	-1.34732	-1.738018
28	H	-4.643472	0.344477	-1.375368
29	C	3.103911	-3.428324	-1.201703
30	H	2.309094	-3.851584	-1.829377
31	H	3.935781	-3.20345	-1.87901
32	C	1.651382	4.568134	-0.123436
33	H	2.524894	4.510815	0.53814
34	H	1.154604	5.515941	0.114822
35	B	0.023545	-0.109717	1.150364
36	C	-2.985121	-3.441619	-1.296836
37	H	-2.168557	-3.85866	-1.900268
38	H	-3.797116	-3.220869	-1.999081
39	C	-1.999728	4.613198	-1.68344
40	H	-1.125414	4.740658	-2.329293

41	H	-2.683818	5.448877	-1.868767
42	H	-2.501734	3.688997	-1.987047
43	C	2.135459	4.610945	-1.587703
44	H	2.657784	3.688242	-1.85985
45	H	2.823074	5.449804	-1.743072
46	H	1.294252	4.729232	-2.277794
47	C	3.556348	-4.49364	-0.18236
48	H	4.384443	-4.123212	0.430486
49	H	3.890723	-5.402981	-0.694275
50	H	2.739385	-4.76358	0.494636
51	C	5.71346	-0.722466	0.409414
52	H	5.429489	-0.033095	1.211123
53	H	6.725764	-0.463977	0.078959
54	H	5.740803	-1.730831	0.834885
55	C	-3.461538	-4.511944	-0.293807
56	H	-2.663971	-4.777194	0.407744
57	H	-3.772938	-5.422886	-0.817168
58	H	-4.311437	-4.148966	0.293222
59	C	-5.663099	-0.733251	0.198956
60	H	-5.705464	-1.738942	0.629662
61	H	-6.661743	-0.479932	-0.174214
62	H	-5.414762	-0.037138	1.006854
63	C	-0.921262	0.106611	3.416442
64	H	-1.027998	1.201695	3.375848
65	H	-0.6647	-0.174073	4.443266
66	H	-1.895874	-0.342941	3.170718
67	H	0.046305	-3.620473	-0.743068
68	H	3.276693	1.948694	0.117513
69	H	-3.219923	1.937942	-0.021737

References:

S1) Oxford Diffraction (2008). CrysAlis CCD and CrysAlis RED. Versions 1.171.33.55. Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.

S2) Sheldrick, G. M.; SHELXS-97 and SHELXL-97, Programs for the Solution and Refinement of Crystal Structures, University of Göttingen, Germany, 1997.

S3) (a) Spek, A. L.; PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2002; (b) Spek, A. L.; *J. Appl. Cryst.* **2003**, *36*, 7-13.

S4) SQUEEZE. Sluis, P. v. d.; Spek, A. L. *Acta Cryst.***1990**, *A46*, 194-201.

S5) WinGX v1.80.05. Farrugia, L. J. *J. Appl. Cryst.* **1999**, *32*, 837-838.

S6) Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.