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NIR absorbing diferrocene-containing *meso*-cyano-BODIPY with a tetracyanotetraferrocenyltetraazaporphyrin-type absorption spectrum

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SUPPORTING INFORMATION

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GENERAL INFORMATION.

Reagents and materials. Solvents were purified using standard approaches: toluene was dried over sodium metal, DCM was dried over calcium hydride. Ferrocene carboxaldehyde was purchased from Sigma Aldrich, BODIPY derivative **3** [1] were prepared as described earlier. All reactions were performed under a dry argon atmosphere.

Spectroscopy Measurements. Jasco-720 spectrophotometer was used to collect UV-Vis data. Electrochemical cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were conducted using a CH Instruments electrochemical analyzer utilizing a three-electrode scheme with platinum working, auxiliary and Ag/AgCl reference electrodes. DCM was used as solvents and 0.05 M solution of tetrabutylammonium tetrakis(pentafluorophenyl)borate (TFAB) was used as supporting electrolyte. In all cases, experimental redox potentials were corrected using decamethylferrocene (Fc*H) as an internal standard. NMR spectra were recorded on a Varian INOVA instrument with a 500 MHz frequency for protons and 125 MHz frequency for carbons. Chemical shifts are reported in parts per million (ppm) and referenced to tetramethylsilane ($Si(CH_3)_4$) as an internal standard. High-resolution mass spectrum of compound **4** was recorded using a Bruker micrOTOF-QIII.

Computational Details. The starting geometry of compound **4** was optimized using a B3LYP exchange-correlation functional.[2] This B3LYP exchange-correlation functional was found to result in good agreement between calculated and experimentally determined bond distances and angles in ferrocene-containing compounds.[3] Energy minima in optimized geometry was confirmed by the frequency calculations (absence of the imaginary frequencies). Solvent effect was calculated using the polarized continuum model (PCM).[4] In all calculations, DCM was used as the solvent. In PCM-TDDFT calculation, the first 50 states were calculated. Full-electron Wachter's basis set [5] was utilized for iron atoms, while all other atoms were modeled using 6-31G(d) [6] basis set. Gaussian 09 software was used in all calculations.[7] QMForge program was used for molecular orbital analysis.[8]

X-ray crystallography. Single crystals of product **4** suitable for X-ray crystallographic analysis were obtained by slow evaporation from a solution of **4** in chloroform-methanol mixture. X-ray diffraction data for **4** were collected on Rigaku RAPID II Image Plate system using graphite-monochromated MoK α radiation (λ = 0.71073 Å) at 123 K. The structure was solved by the Patterson method (SHELXS 86) and refined by full-matrix least-squares refinement on F^2 using SHELXL-2014/7 (Sheldrick, 2014) and the user interface ShelXle. [9,10] Crystal data for **4**

$C_{52}H_{42}B_1F_2Fe_2N_3O_4$: M 933.39, triclinic, space group P-1, a = 12.5670(5), b = 13.2195(5), c = 14.1831(10) Å, α = 114.172(8) °, β = 93.299(7) °, γ = 97.933(7)°, V = 1040.45(7) Å^3, Z = 2, μ = 0.748 mm-1, 9537 reflections, (6269 I > 2.0/s(I)), θ_{max} = 27.461; final R_1 = 0.0491, R_w = 0.1608. Additional crystallographic information may be found in the cif, CCDC-1494012

EXPERIMENTAL PROCEDURE.

Compound 4. The mixture of compound **3** (170 mg, 0.3 mmol), ferrocene carboxaldehyde (135 mg, 0.63 mmol), acetic acid (226 mg, 12eq) and piperidine (0.62 mmol, 53 mg) in toluene (10 mL) was refluxed for 30 min. Then the solution was washed with water, organic layer was dried over Na_2SO_4 and evaporated to dryness. The crude was purified by column chromatography on silica gel using DCM as a solvent yielding 80 mg (27 %) of compound **4**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 – 8.07 (m, 1H), 7.77 (d, $^3J_{H,H}$ = 16.0 Hz, 1H), 7.55-7.49 (m, 2H), 7.42 (d, $^3J_{H,H}$ = 16.0 Hz, 1H), 7.33-7.31 (m, 6H), 7.25-7.24 (m, 1H), 4.73 (t, $^3J_{H,H}$ = 1.8 Hz, 4H), 4.64 (t, $^3J_{H,H}$ = 1.8 Hz, 4H), 4.31 (s, 10H), 4.05 (q, $^3J_{H,H}$ = 7.1 Hz, 4H), 0.90 (t, $^3J_{H,H}$ = 7.1 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.71, 152.12, 150.84, 145.76, 144.86, 141.40, 136.43, 135.67, 131.73, 129.92, 129.45, 129.16, 128.07, 126.94, 126.08, 115.23, 111.82, 102.45, 82.65, 72.68, 70.76, 69.37, 61.21, 13.67; : λ_{max} (CH_2Cl_2)/nm 340, 367, 449, 654 and 925 (ε/dm^3 mol^{-1} cm^{-1} 29 700, 29 800, 26 300, 39 000 and 27 000); HRMS (ESI positive) calcd for $C_{52}H_{42}BF_2Fe_2N_3O_3$ [M + H]+: 934.1736, found 934.2045.

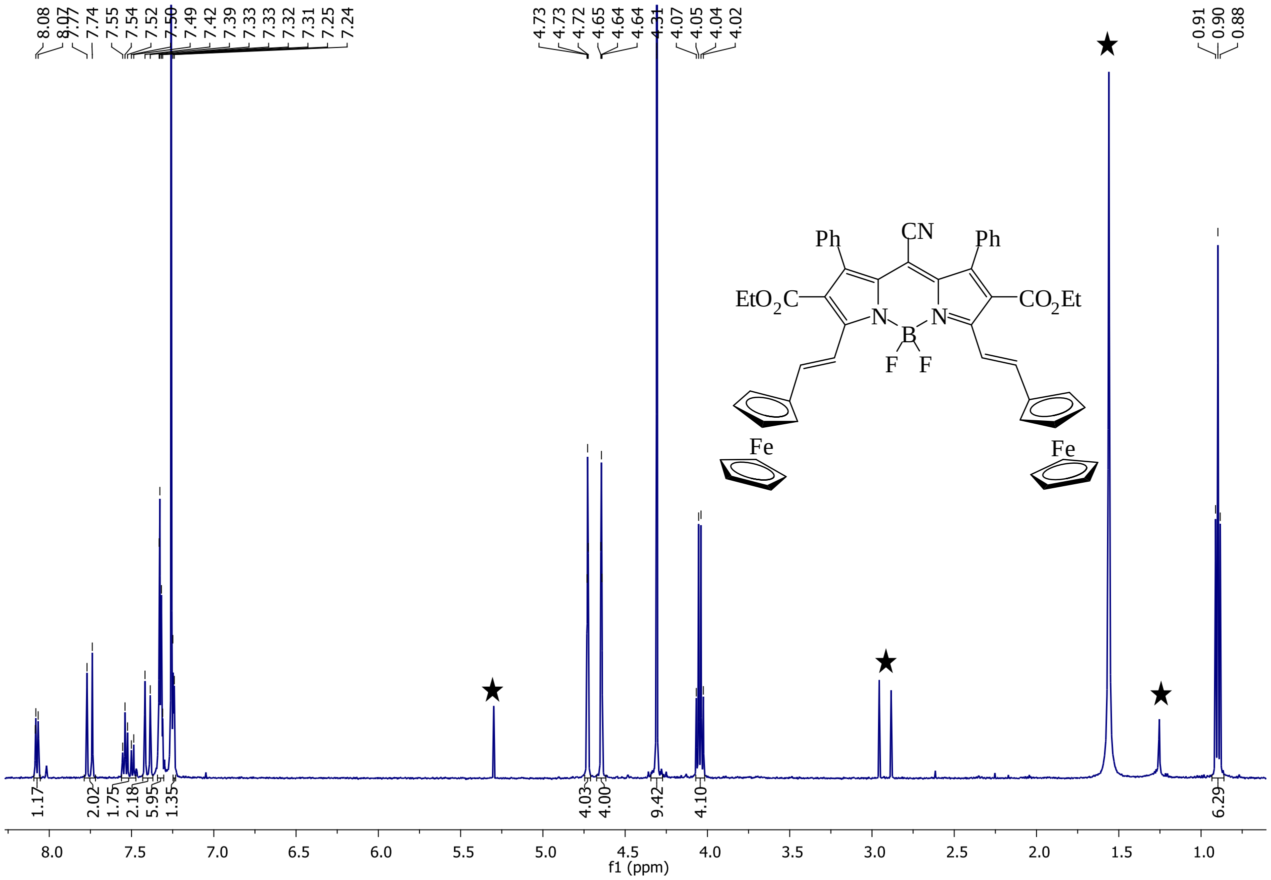

Figure S1. ^{1}H NMR spectrum of compound **4** in $CDCl_3$. (★denote solvent residues).

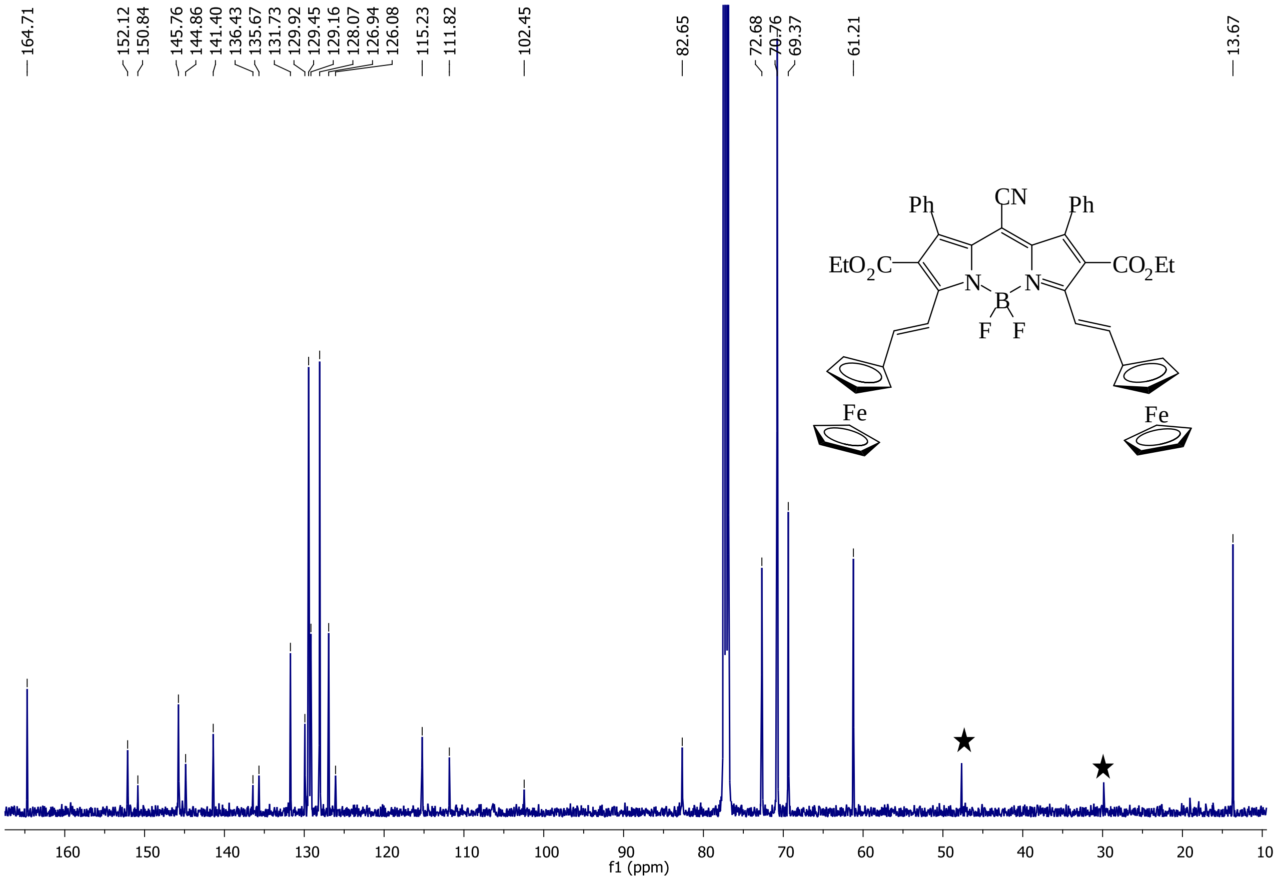

Figure S2. ^{13}C NMR spectrum of compound **4** in $CDCl_3$. (★denote solvent residues).

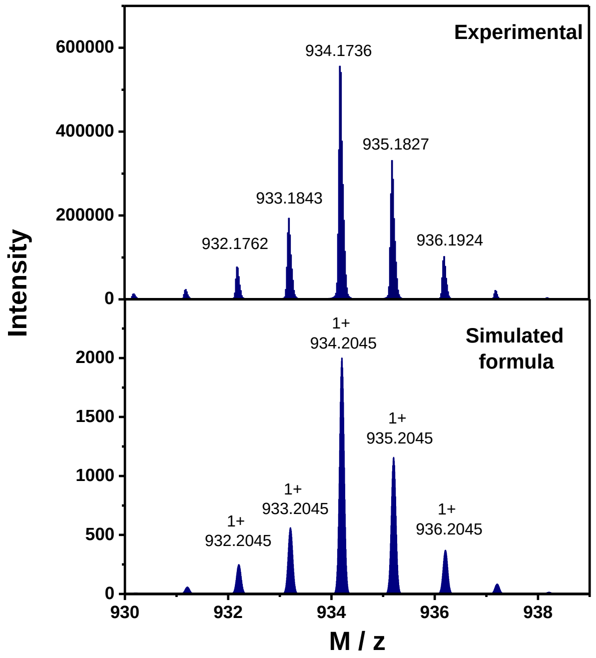

Figure S3. HRMS spectrum of compound **4**.

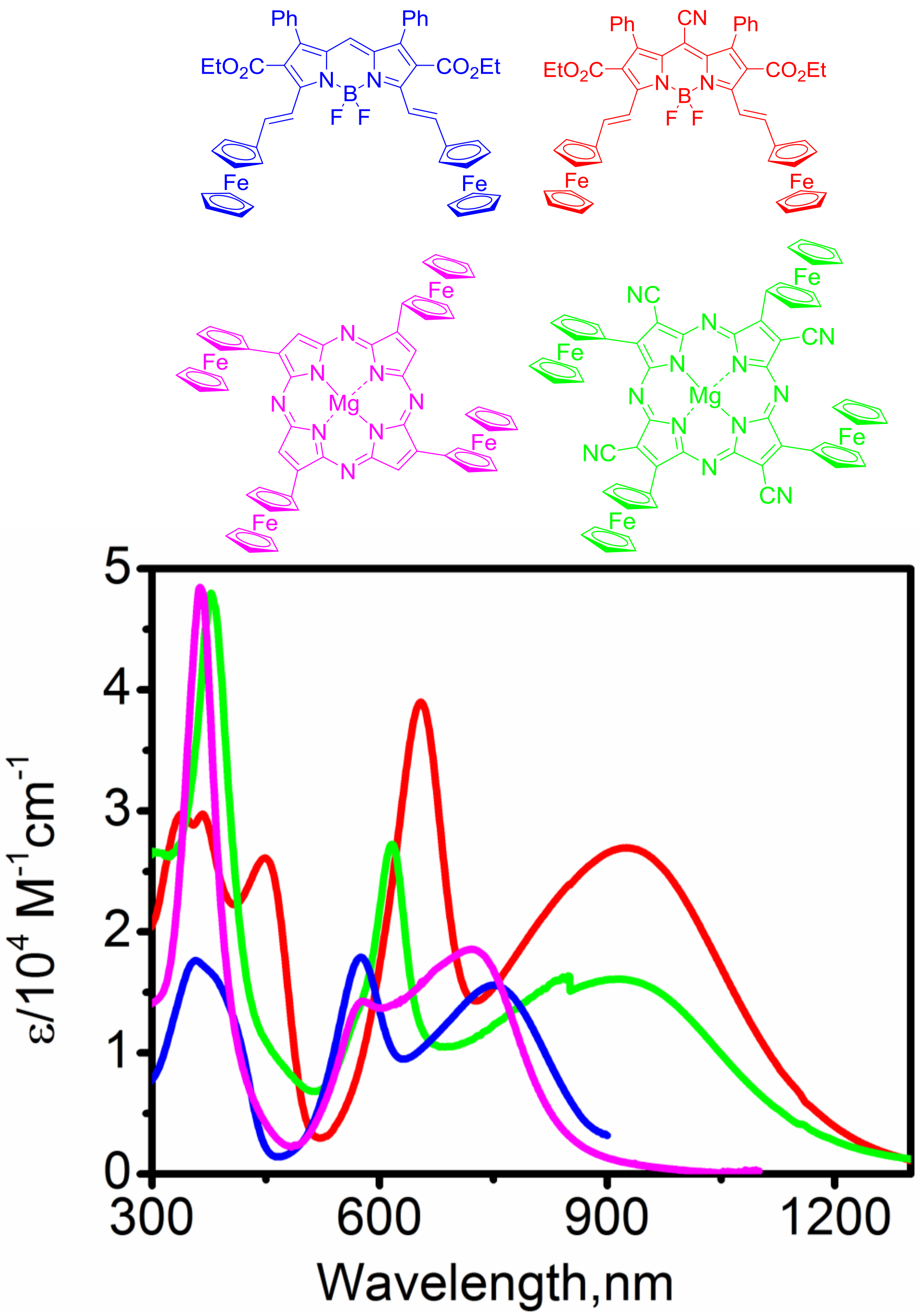

Figure S4. UV-Vis-NIR spectra of compounds **4 - 7**.

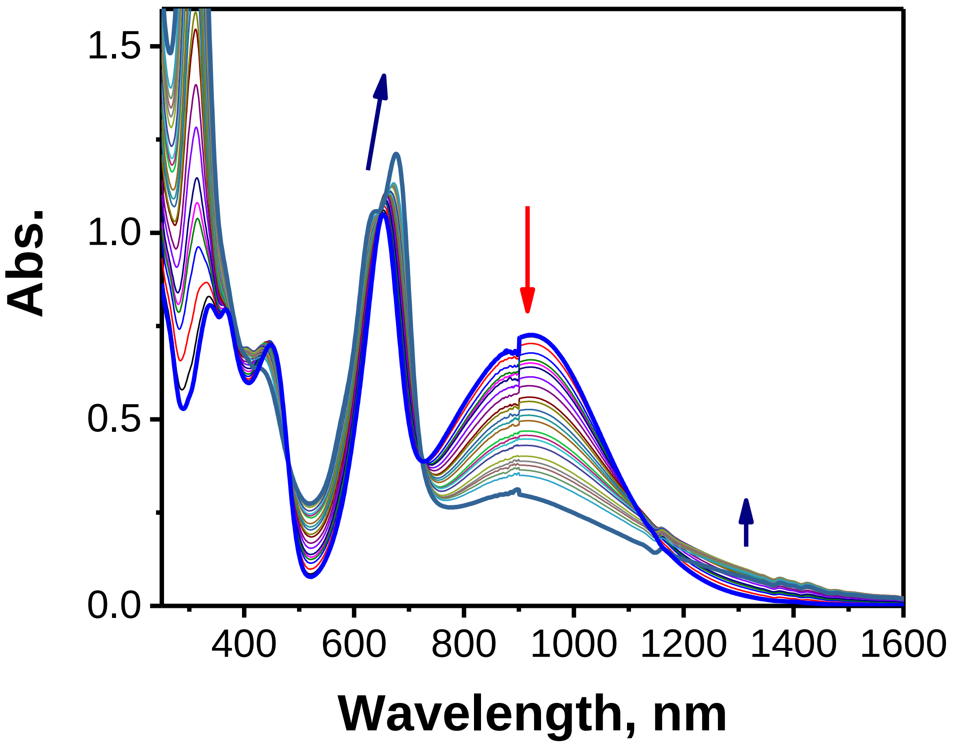

Figure S5. Oxidative titration of compound **4** with iron (III) perchlorate.

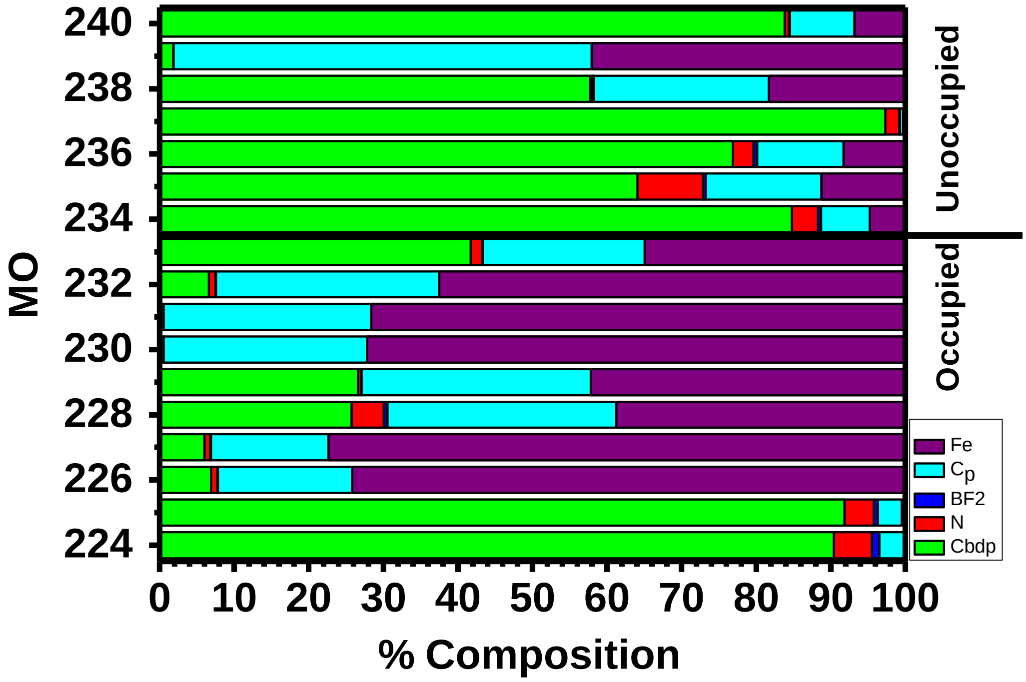

Figure S6. DFT-predicted molecular orbital compositions for BODIPY **4.** Contributions from iron are in violet color, from cyclopentadiene ligands are in cyan, from BF_2 fragment are in blue, from nitrogens are in red, and from the rest of BODIPY core are in green.

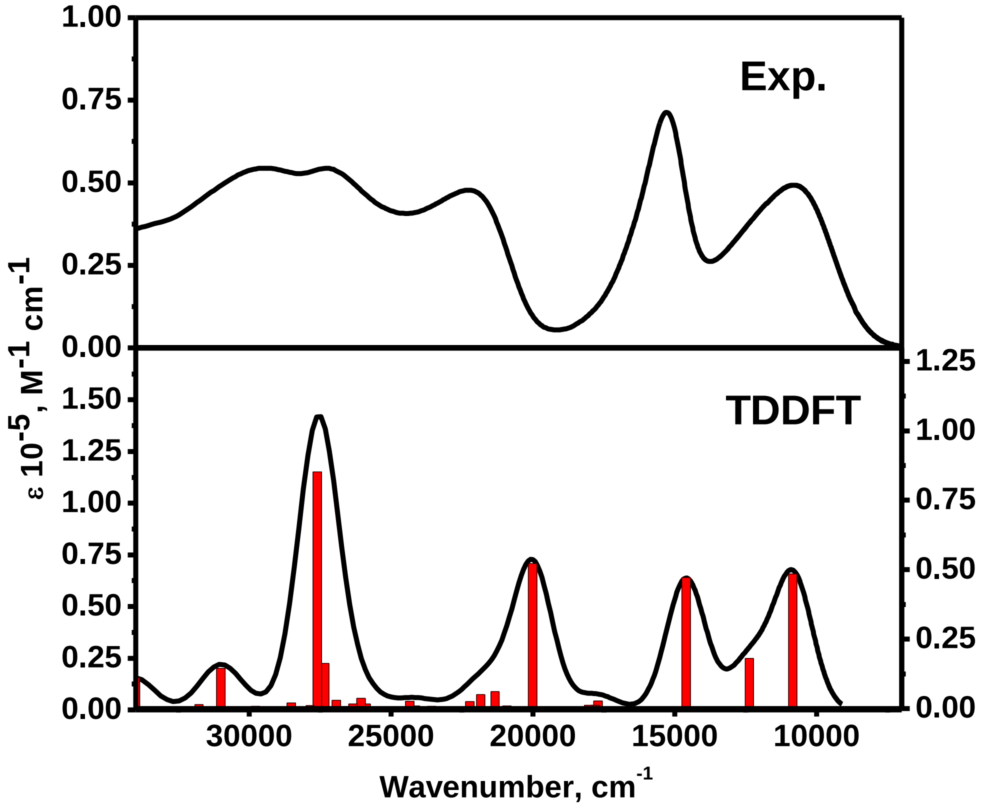

Figure S7. DFT predicted absorption spectra of compound **4** in energy scale.

Table S1. Redox properties of BODIPYs **4** and **5** in DCM. [a]

Dye	Oxidation			Reduction	
	$E_{1/2}^{Ox3}$, V	$E_{1/2}^{Ox2}$, V	$E_{1/2}^{Ox1}$, V	$E_{1/2}^{red1}$, V	$E_{1/2}^{red2}$, V
4[b]	~1.3 (irr)	0.25	0.05	-0.85	-1.56
5[b]	~1.3 (irr)	0.17	0.02	-1.21	

[a] All potentials are referred to the FcH/FcH+ couple.

[b]DCM/0.05 M TBAB(C_6F_5)$_4$ system.

Table S2. Compositions of the frontier MOs of organometallic BODIPY **4** predicted by DFT-PCM calculations.[a]

Compound **4**						
		Composition				
MO	E, eV	C_{bdp}	N	BF_2	C_p	Fe
214	-7.702	0.97	0.12	0.02	71.49	27.39
215	-7.652	30.85	2.49	0.76	47.33	18.57
216	-7.636	17.26	1.37	0.41	58.19	22.77
217	-7.514	51.93	18.23	1.38	20.94	7.51
218	-7.453	12.28	2.56	0.24	64.24	20.69
219	-7.204	72.64	2.16	0.08	23.14	1.97
220	-7.164	97.73	0.12	0.02	1.97	0.15
221	-7.144	52.71	2.22	0.05	42.22	2.79
222	-7.119	7.45	0.5	0.01	87.23	4.8
223	-7.061	3.87	0.41	0.06	90.43	5.23
224	-7.052	90.43	5.1	1.02	3.24	0.21
225	-6.907	91.83	3.94	0.55	3.24	0.43
226	-6.713	6.9	0.81	0.09	18.03	74.16
227	-6.643	6.02	0.76	0.1	15.79	77.33
228	-6.528	25.77	4.29	0.51	30.69	38.73
229	-5.939	26.63	0.45	0.03	30.71	42.16
230	-5.813	0.55	0	0	27.28	72.17
231	-5.735	0.55	0	0	27.84	71.61
232	-5.712	6.6	0.88	0.09	29.93	62.5
233	**-5.434**	**41.72**	**1.57**	**0.05**	**21.69**	**34.97**
234	**-3.709**	**84.77**	**3.51**	**0.42**	**6.52**	**4.78**
235	-1.672	64.09	8.76	0.38	15.51	11.25
236	-1.569	76.87	2.78	0.48	11.6	8.27
237	-0.722	97.33	1.86	0.08	0.43	0.3
238	-0.636	57.73	0.3	0.21	23.43	18.32
239	-0.622	1.85	0.03	0.01	56.06	42.05
240	-0.601	83.81	0.56	0.17	8.66	6.8
241	-0.584	36.06	0.11	0.04	35.33	28.46
242	-0.547	16.58	0.05	0.03	46.1	37.24
243	-0.43	49.25	0.52	0.08	28.72	21.43
244	-0.41	69.12	0.56	0.09	17.89	12.35
245	-0.267	52.65	0.94	0.12	13.32	32.97
246	-0.23	10.99	0.36	0.13	10.9	77.62
247	-0.09	25.97	0.38	0.18	12.81	60.67
248	-0.023	12.35	0.14	0.03	7.73	79.74
249	0.398	91.09	3.49	0.17	4.02	1.23
250	0.534	79.3	4.15	2.61	9.86	4.08
251	0.796	81.26	6.64	0.54	8.83	2.73
252	0.977	56.61	0.13	0.34	32.71	10.21
253	1.205	89.61	1.13	0.14	6.1	3.02

[a] HOMO and LUMO are in bold font.

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