Supplementary Information (SI) for New Journal of Chemistry.

Tuning the Electronic Structure of BODIPY-Coumarin Ratiometric Fluorescent Sensors for Accurate Microviscosity Monitoring Applications.

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S1. DFT Computations

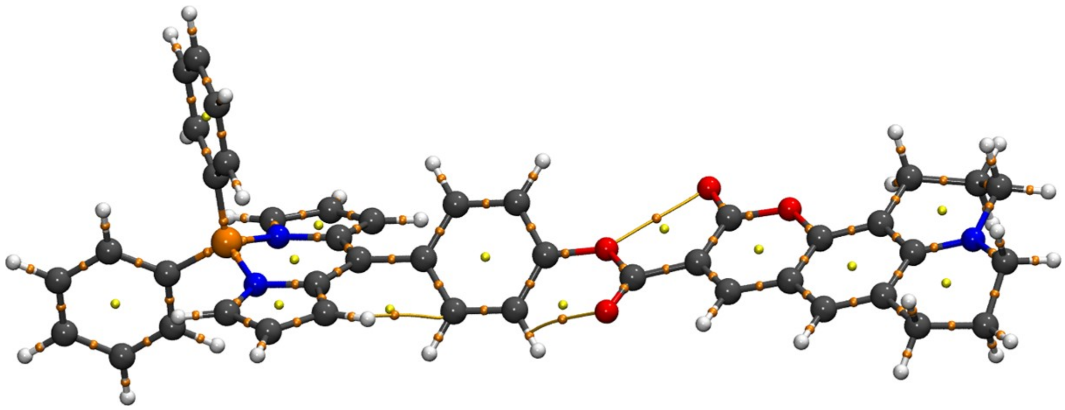


Figure S1. Molecular graph for **FMR-II** at the M06-2X/6-31+G** level of theory in vacuum, with bond critical points (3, -1) in orange and ring critical points (3, +1) in yellow.

Optimized coordinates

FMR-I							
In vacuum				**In dimethylsulfoxide (PCM)**			
E(RM062X) = -2072.18720204 Ha				E(RM062X) = -2072.21416161 Ha			
O	-2.24960	-0.34060	-0.25440	O	-2.24500	-0.82870	0.28490
N	5.49160	-0.98110	-0.86900	C	4.16230	-1.13670	0.81780
C	4.10170	-1.00320	-0.84200	N	5.36240	0.30710	-1.27370
C	5.90690	-2.06350	-1.52440	C	6.04130	-1.87510	1.70170
H	6.96460	-2.24200	-1.67310	H	7.11040	-1.97320	1.84400
N	5.42800	1.30930	0.04770	C	-3.03030	-0.00650	-0.45030
C	-3.10380	0.67950	-0.03070	O	-2.57710	0.83310	-1.19870
O	-2.75550	1.81550	0.19310	N	-10.84010	0.25240	0.07700
C	-11.97340	0.87390	0.15970	C	-11.82350	1.12240	-0.56780
H	-12.84350	0.48040	-0.37620	H	-12.75560	0.55380	-0.63170
H	-11.67970	1.78400	-0.37130	H	-11.51640	1.32060	-1.59750
C	-12.34490	1.17640	1.61040	C	-12.05230	2.41980	0.20330
H	-12.68640	0.26760	2.11490	H	-12.39470	2.20420	1.21960
H	-13.14820	1.91710	1.65790	H	-12.81310	3.02660	-0.29480
H	-11.48280	1.56130	2.16210	H	-11.13100	3.00520	0.27070
C	4.80180	-2.83290	-1.95410	C	4.99080	-2.53790	2.37680
H	4.85350	-3.74750	-2.52620	H	5.11030	-3.27810	3.15430
O	-4.27430	-2.08020	-0.58040	O	-4.43050	-2.20460	1.11270
N	-10.91280	-0.11910	0.04310	C	10.13140	-0.20480	-0.99540
C	10.11790	0.86020	-0.87340	H	11.02230	0.41410	-0.93580
H	11.06780	0.92120	-0.34950	C	8.91500	0.27120	-0.49660
C	8.96220	0.49230	-0.17940	H	8.87760	1.26250	-0.05010
H	9.02930	0.26880	0.88300	C	6.37540	1.40170	0.86020
C	6.54520	-0.57100	1.45570	C	7.05520	1.38400	2.09000
C	7.29190	-1.74630	1.63620	H	7.54330	0.46700	2.41870
H	7.75540	-2.22240	0.77270	C	7.13360	2.51060	2.90690
C	7.47220	-2.32030	2.89210	H	7.67090	2.46170	3.85000
H	8.06010	-3.22820	2.99480	C	6.52180	3.70250	2.51100
C	6.89870	-1.72660	4.01770	H	6.57690	4.58390	3.14320
H	7.03490	-2.16910	5.00010	C	5.83810	3.74760	1.29820
C	6.15050	-0.56300	3.86720	H	5.35460	4.66740	0.98040
H	5.69560	-0.09280	4.73470	C	5.76870	2.60910	0.48870
C	5.97890	0.00300	2.60100	H	5.22460	2.67450	-0.45200

H	5.38590	0.91220	2.51600	C	10.20090	-1.47270	-1.56940
C	10.05350	1.14590	-2.23470	H	11.14390	-1.84820	-1.95580
H	10.95020	1.42840	-2.77850	N	5.55040	-1.04760	0.77870
C	3.66560	-2.16720	-1.52840	C	3.80870	-2.07630	1.82230
H	2.63450	-2.43390	-1.71440	H	2.80190	-2.39170	2.05920
O	-6.33280	-1.32520	-0.35290	O	-6.39770	-1.31080	0.71600
C	-4.95570	-1.11920	-0.35420	C	-5.02390	-1.30010	0.56950
C	-6.84800	0.96170	0.14290	C	-6.72090	0.63420	-0.64830
C	-0.12870	-1.14120	0.34610	C	-0.13640	-0.28030	1.23680
H	-0.64370	-1.96650	0.82540	H	-0.65250	0.00320	2.14760
C	1.89650	0.01320	-0.30760	C	1.89690	-0.57560	-0.04810
C	5.79420	2.52740	0.44750	C	5.66850	0.96900	-2.39210
H	6.84350	2.78900	0.50830	H	6.70160	1.17600	-2.64320
C	1.11710	1.00770	-0.91150	C	1.13410	-1.01240	-1.14070
H	1.60600	1.83030	-1.42420	H	1.63010	-1.32000	-2.05580
C	-11.33500	-1.50590	-0.10940	C	-11.37630	-0.75240	0.99350
H	-12.31280	-1.60150	0.37410	H	-12.31150	-0.35270	1.39530
H	-10.65490	-2.15360	0.45190	H	-10.69880	-0.86320	1.84410
C	4.04100	1.24120	0.08940	C	3.97690	0.21680	-1.19340
C	4.65600	3.30010	0.76600	C	4.49250	1.33200	-3.08340
H	4.66320	4.32470	1.10780	H	4.45060	1.86540	-4.02180
C	-0.27150	0.93690	-0.89850	C	-0.25030	-1.08990	-1.04880
H	-0.86920	1.70370	-1.37380	H	-0.84690	-1.43930	-1.88450
C	-11.42980	-1.94060	-1.57110	C	-11.62870	-2.09300	0.30700
H	-11.75400	-2.98260	-1.64260	H	-12.03850	-2.81250	1.02060
H	-10.46340	-1.84310	-2.07290	H	-10.70330	-2.50350	-0.10660
H	-12.15200	-1.31900	-2.10870	H	-12.34490	-1.97300	-0.51100
C	3.55180	2.48870	0.55450	C	3.42620	0.87220	-2.32440
H	2.51120	2.74100	0.70210	H	2.37310	0.97310	-2.54660
C	-0.88130	-0.13880	-0.25750	C	-0.86840	-0.71110	0.13840
C	3.37300	0.08250	-0.33830	C	3.37040	-0.48580	-0.13830
C	1.25820	-1.06740	0.31480	C	1.25100	-0.22270	1.14320
H	1.85490	-1.83900	0.79190	H	1.83560	0.11980	1.99140
C	7.71990	0.40170	-0.82030	C	7.74420	-0.49650	-0.55710
C	-5.45560	1.23260	0.15560	C	-5.32360	0.70000	-0.81450
H	-5.09900	2.24090	0.35560	H	-4.89040	1.49570	-1.41600
C	-4.52730	0.26030	-0.07700	C	-4.47580	-0.20720	-0.22800
C	-7.86040	1.91480	0.37040	C	-7.64900	1.54220	-1.20990
H	-7.57500	2.94180	0.58190	H	-7.27820	2.35490	-1.82780
C	7.68160	0.70300	-2.19220	C	7.84120	-1.76910	-1.14620
H	6.73020	0.65110	-2.72040	H	6.94980	-2.39160	-1.21440
C	-7.25220	-0.35880	-0.11680	C	-7.23930	-0.39930	0.15510
C	-9.19020	1.57080	0.34040	C	-8.99440	1.42160	-0.98000
H	-9.93150	2.33270	0.54160	H	-9.66520	2.15110	-1.41350
C	8.82680	1.06750	-2.89600	C	9.04770	-2.25780	-1.64500
H	8.76570	1.29230	-3.95720	H	9.09250	-3.24700	-2.09210
C	-8.58390	-0.73500	-0.15670	C	-8.58750	-0.55090	0.40580
H	-8.80510	-1.76810	-0.38880	H	-8.90050	-1.38770	1.01560
C	-9.59230	0.22530	0.07270	C	-9.51130	0.36570	-0.15680
B	6.35380	0.04100	-0.03860	B	6.31170	0.05110	-0.04910

FMR-II

In vacuum E(RM062X) = -2148.40167555 Ha				**In dimethylsulfoxide (PCM)** E(RM062X) = -2148.42759972 Ha			
O	-1.95930	-0.29420	-0.55570	O	-1.98180	-1.01060	0.20080
C	4.43230	-0.81480	-1.09940	C	4.44560	-1.25110	0.62760
N	5.67400	1.31350	0.24990	N	5.57040	0.57050	-1.19960
C	6.28980	-1.72100	-1.85960	C	6.35310	-2.09250	1.34000
H	7.35710	-1.86220	-1.97750	H	7.42610	-2.19620	1.44240
C	-2.81730	0.67660	-0.17840	C	-2.74850	0.09010	0.01160
O	-2.47660	1.78940	0.15010	O	-2.26890	1.18080	-0.21900
N	-10.59680	-0.24230	0.19040	N	-10.56830	0.16630	-0.03660
C	-11.60740	0.65820	0.72590	C	-11.51180	1.26850	-0.21310
H	-11.66510	0.56830	1.82420	H	-11.74960	1.71810	0.76310
H	-12.57380	0.34280	0.32100	H	-12.43600	0.84320	-0.61320
C	-11.30830	2.09760	0.33720	C	-10.95680	2.32250	-1.15580
H	-12.08820	2.75540	0.73100	H	-11.67520	3.14120	-1.24480
H	-11.31610	2.18090	-0.75530	H	-10.82020	1.88390	-2.15080
C	5.22230	-2.40890	-2.48110	C	5.32770	-2.87080	1.92280
H	5.32140	-3.20440	-3.20480	H	5.47450	-3.72140	2.57240

O	-3.96400	-2.08380	-0.78460	O	-4.19490	-2.48410	0.72750
C	10.43920	0.92200	-0.34050	C	10.27550	0.01170	-1.45310
H	11.34500	0.84010	0.25380	H	11.15220	0.65300	-1.43340
C	9.22530	0.45640	0.17120	C	9.11120	0.39960	-0.78450
H	9.20160	0.01330	1.16430	H	9.10110	1.34550	-0.24720
C	6.67870	-0.79620	1.39350	C	6.74060	1.24210	1.03010
C	7.34840	-2.03020	1.40200	C	7.60480	1.03870	2.11940
H	7.82020	-2.38820	0.48750	H	8.17700	0.11360	2.18160
C	7.43950	-2.81200	2.55060	C	7.76460	1.99200	3.12330
H	7.97010	-3.75970	2.52210	H	8.44630	1.80380	3.94820
C	6.85010	-2.37550	3.73810	C	7.05120	3.19180	3.06470
H	6.91560	-2.98040	4.63770	H	7.17220	3.94000	3.84240
C	6.17510	-1.15860	3.75660	C	6.18410	3.41850	1.99830
H	5.70830	-0.80960	4.67360	H	5.62150	4.34640	1.94300
C	6.09260	-0.38360	2.59660	C	6.03550	2.45290	0.99700
H	5.55410	0.56140	2.64150	H	5.35140	2.65830	0.17510
C	10.48880	1.49060	-1.61040	C	10.31280	-1.19910	-2.14270
H	11.43100	1.85210	-2.01210	H	11.21630	-1.50700	-2.66100
N	5.82100	-0.77840	-1.04420	N	5.83130	-1.13600	0.57130
C	4.05340	-1.84050	-2.00510	C	4.12700	-2.34550	1.47450
H	3.03790	-2.07820	-2.29050	H	3.12980	-2.70850	1.68190
O	-6.02310	-1.36650	-0.45980	O	-6.15180	-1.52170	0.45560
C	-4.65140	-1.13950	-0.50710	C	-4.77270	-1.45780	0.44340
C	-6.55650	0.88900	0.14220	C	-6.43040	0.78350	-0.13600
C	0.15770	-1.18460	-0.10130	C	0.12910	-0.57010	1.24810
H	-0.36270	-2.08070	0.21910	H	-0.37950	-0.45040	2.19870
C	2.18580	0.07450	-0.50210	C	2.15150	-0.59440	-0.08750
C	6.00190	2.44920	0.86680	C	5.83150	1.44650	-2.17290
H	7.04250	2.69730	1.03600	H	6.85340	1.71630	-2.41010
C	1.41140	1.15300	-0.94630	C	1.38750	-0.86740	-1.23000
H	1.90440	2.05390	-1.29870	H	1.87850	-1.00390	-2.18830
C	-10.95020	-1.65440	0.15560	C	-11.12570	-1.08080	0.48030
H	-12.00980	-1.72170	-0.10790	H	-12.14670	-1.16550	0.10080
H	-10.82710	-2.10710	1.15400	H	-11.18060	-1.03840	1.57890
C	4.28750	1.23650	0.19690	C	4.18960	0.44070	-1.09960
C	4.83800	3.15700	1.23840	C	4.62970	1.91760	-2.74400
H	4.81260	4.11120	1.74380	H	4.55120	2.62630	-3.55550
C	0.02290	1.07710	-0.97230	C	0.00590	-0.99700	-1.13820
H	-0.57140	1.91290	-1.31660	H	-0.59600	-1.22280	-2.01200
C	-10.09570	-2.39310	-0.86300	C	-10.28870	-2.26970	0.03790
H	-10.39200	-3.44510	-0.90240	H	-10.72670	-3.19180	0.42810
H	-10.27470	-1.95740	-1.85230	H	-10.30410	-2.32770	-1.05620
C	3.75760	2.38890	0.83150	C	3.59430	1.29530	-2.06240
H	2.70760	2.61240	0.95750	H	2.53310	1.41750	-2.22780
C	-0.59120	-0.09250	-0.53000	C	-0.60500	-0.83680	0.09950
C	3.66050	0.16230	-0.45630	C	3.62170	-0.45610	-0.18060
C	1.54410	-1.10200	-0.09350	C	1.51250	-0.45750	1.15190
H	2.13820	-1.94120	0.25540	H	2.09900	-0.23790	2.03860
C	8.03710	0.54660	-0.56510	C	7.95850	-0.39880	-0.78730
C	-5.16910	1.18170	0.10690	C	-5.02890	0.90000	-0.16660
H	-4.82130	2.18710	0.33530	H	-4.57610	1.85750	-0.41340
C	-4.23460	0.23630	-0.20150	C	-4.19850	-0.16280	0.09870
C	-7.56310	1.81900	0.46060	C	-7.32810	1.84010	-0.40780
H	-7.27510	2.84220	0.69370	H	-6.92220	2.82020	-0.64820
C	8.11370	1.12990	-1.84100	C	8.02180	-1.61090	-1.49550
H	7.20600	1.22130	-2.43650	H	7.14450	-2.25560	-1.52590
C	-6.95170	-0.42430	-0.15180	C	-6.97990	-0.47380	0.17610
C	-8.89240	1.46780	0.49890	C	-8.68710	1.66480	-0.36220
C	9.31800	1.59520	-2.36350	C	9.17810	-2.01320	-2.16280
H	9.34710	2.03980	-3.35450	H	9.19640	-2.95750	-2.69970
C	-8.27980	-0.83360	-0.14620	C	-8.34140	-0.72110	0.21770
C	-9.26860	0.12120	0.18680	C	-9.22120	0.36280	-0.05550
B	6.60970	0.07180	0.01940	B	6.57640	0.07780	-0.09670
C	-8.62330	-2.26320	-0.49080	C	-8.85790	-2.10420	0.53510
H	-8.39170	-2.91020	0.36540	H	-8.81890	-2.27210	1.61920
H	-7.98140	-2.60340	-1.30800	H	-8.20200	-2.85210	0.08160
C	-9.94130	2.48560	0.88680	C	-9.62440	2.82220	-0.61250
H	-9.64140	3.47490	0.52750	H	-9.15550	3.53010	-1.30160
H	-10.00120	2.55140	1.98140	H	-9.80110	3.35970	0.32830

S2. NMR and HRMS Spectra

8-(4-hydroxyphenyl)-4,4-diphenyl-BODIPY (**2**).

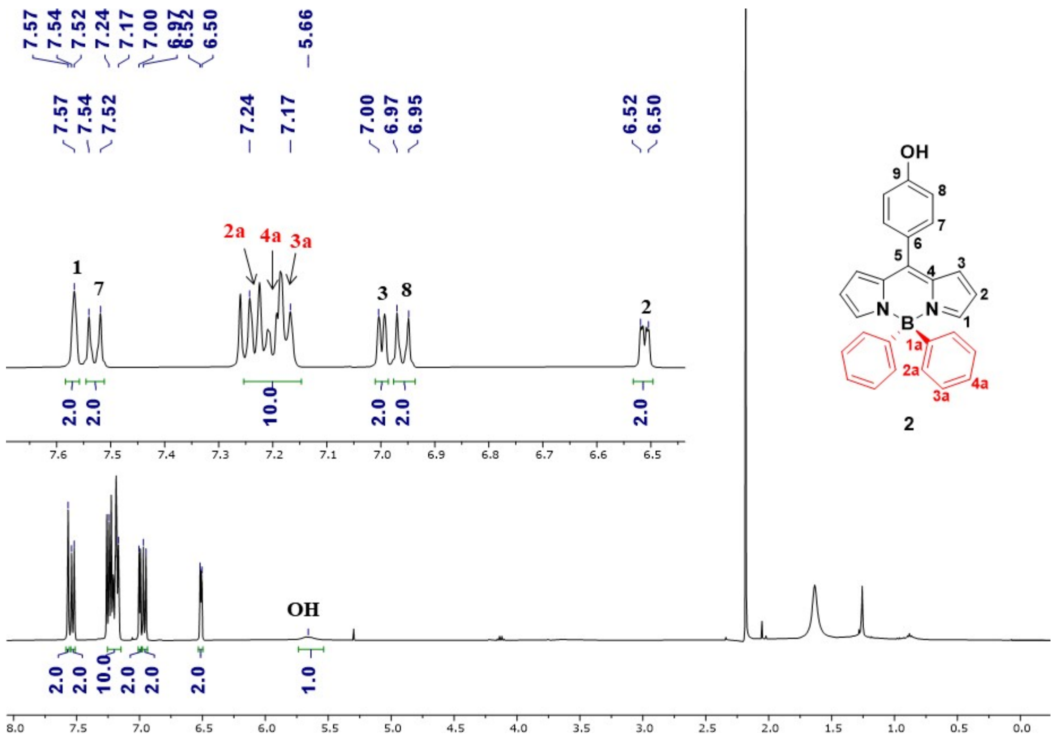


Figure S2. ^{1}H-NMR spectrum for **2** ($CDCl_3$, 400 MHz).

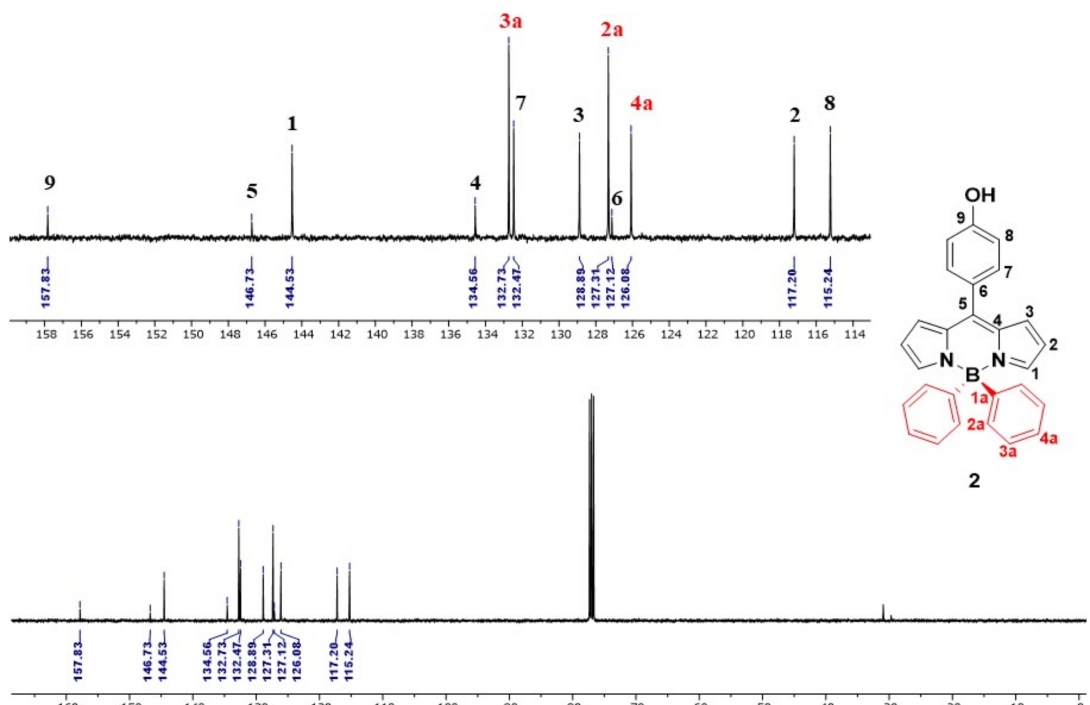
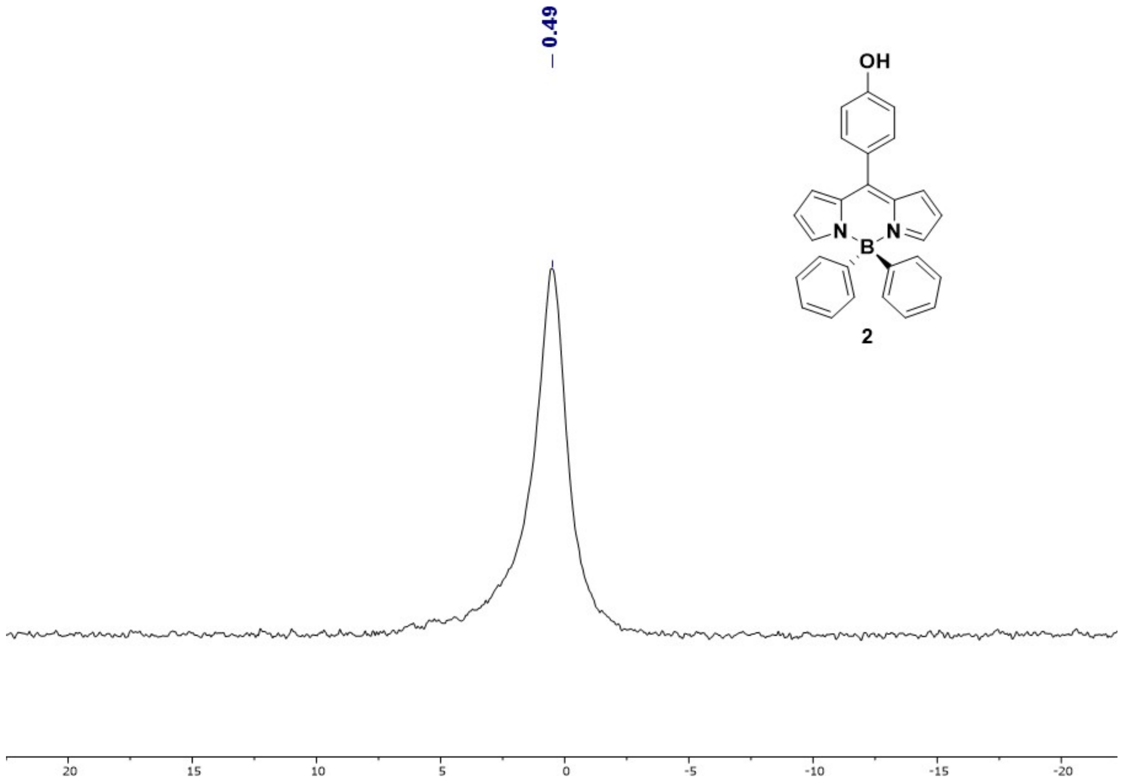
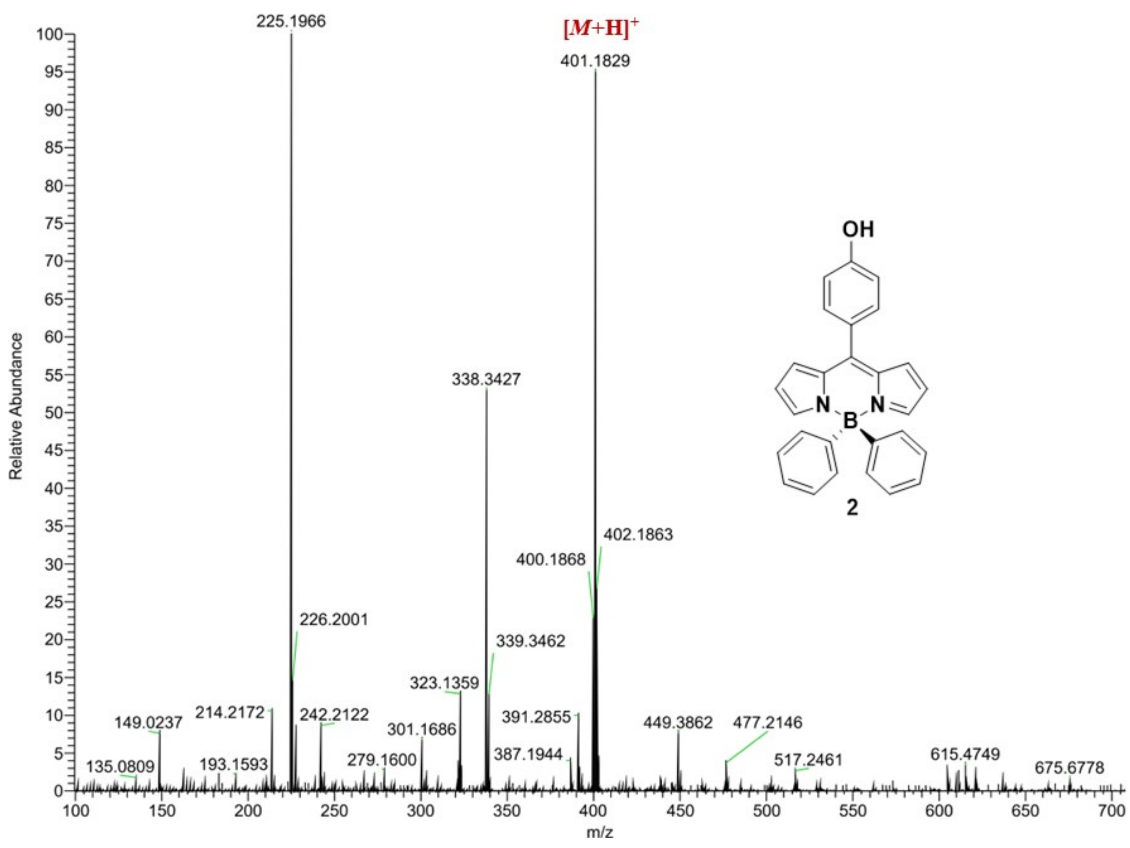


Figure S3. ^{13}C-NMR spectrum for **2** ($CDCl_3$, 100 MHz).



2

Figure S4. ^{11}B-NMR spectrum for **2** ($CDCl_3$, 128 MHz).



2

Figure S5. **HRMS** (ESI-TOF$^+$) spectrum for **2**.

Fluorescent Molecular Rotor I **(FMR-I)**.

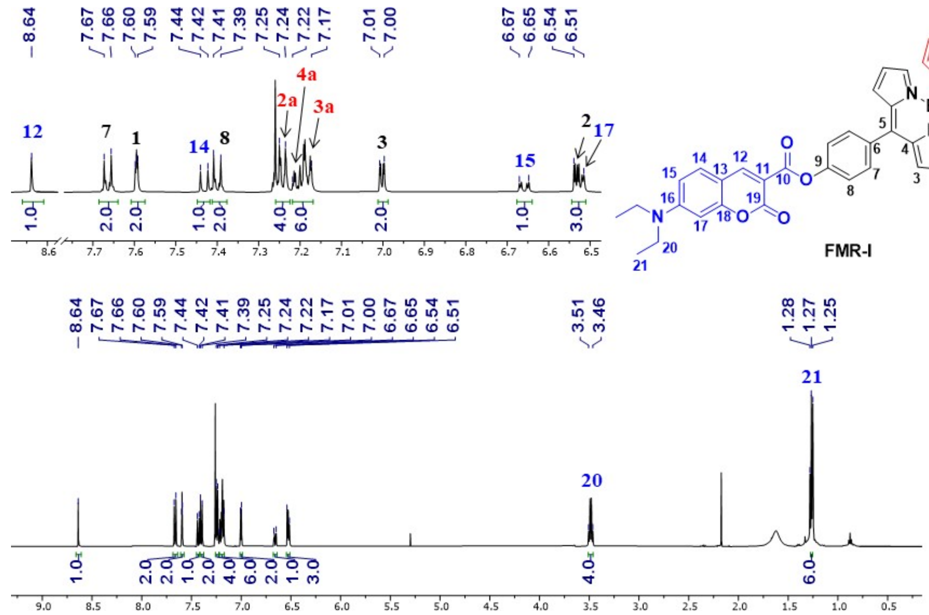


Figure S6. ^{1}H-NMR spectrum for **FMR-I** ($CDCl_3$, 500 MHz).

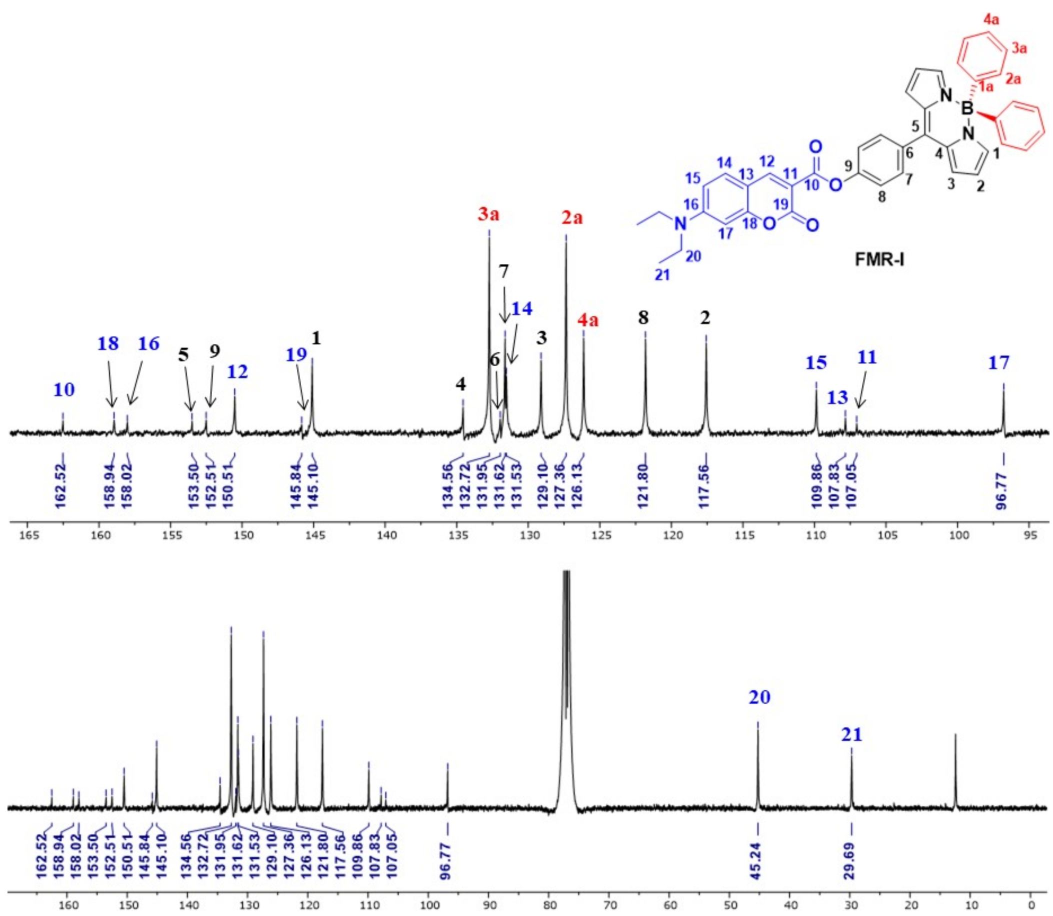


Figure S7. ^{13}C-NMR spectrum for **FMR-I** ($CDCl_3$, 125 MHz).

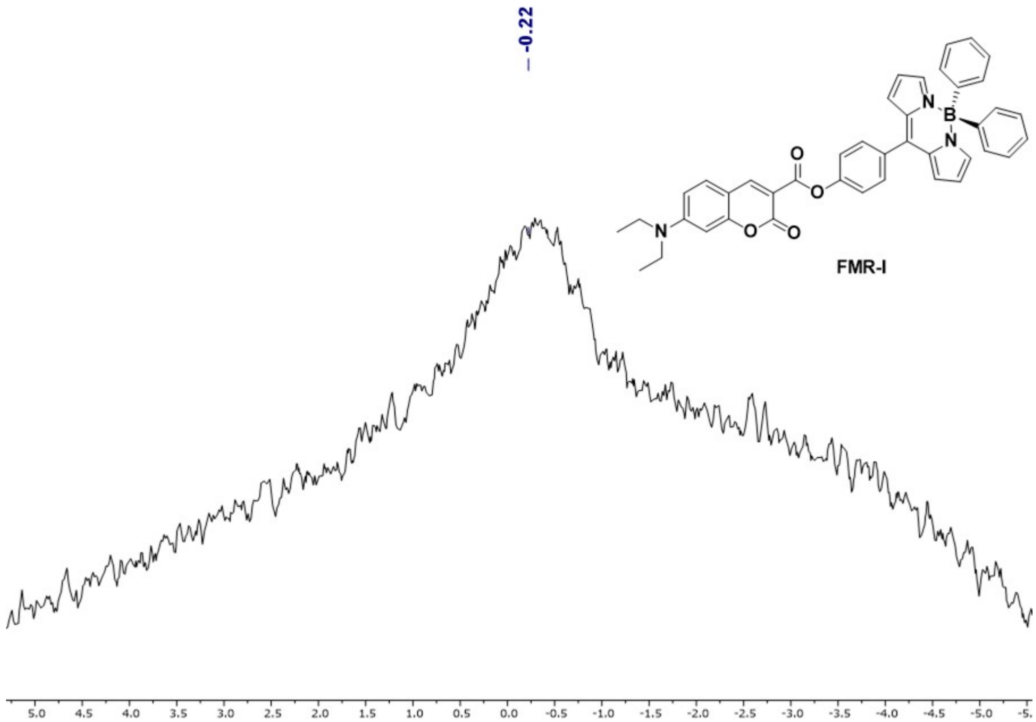


Figure S8. ^{11}B-NMR spectrum for **FMR-I** ($CDCl_3$, 128 MHz).

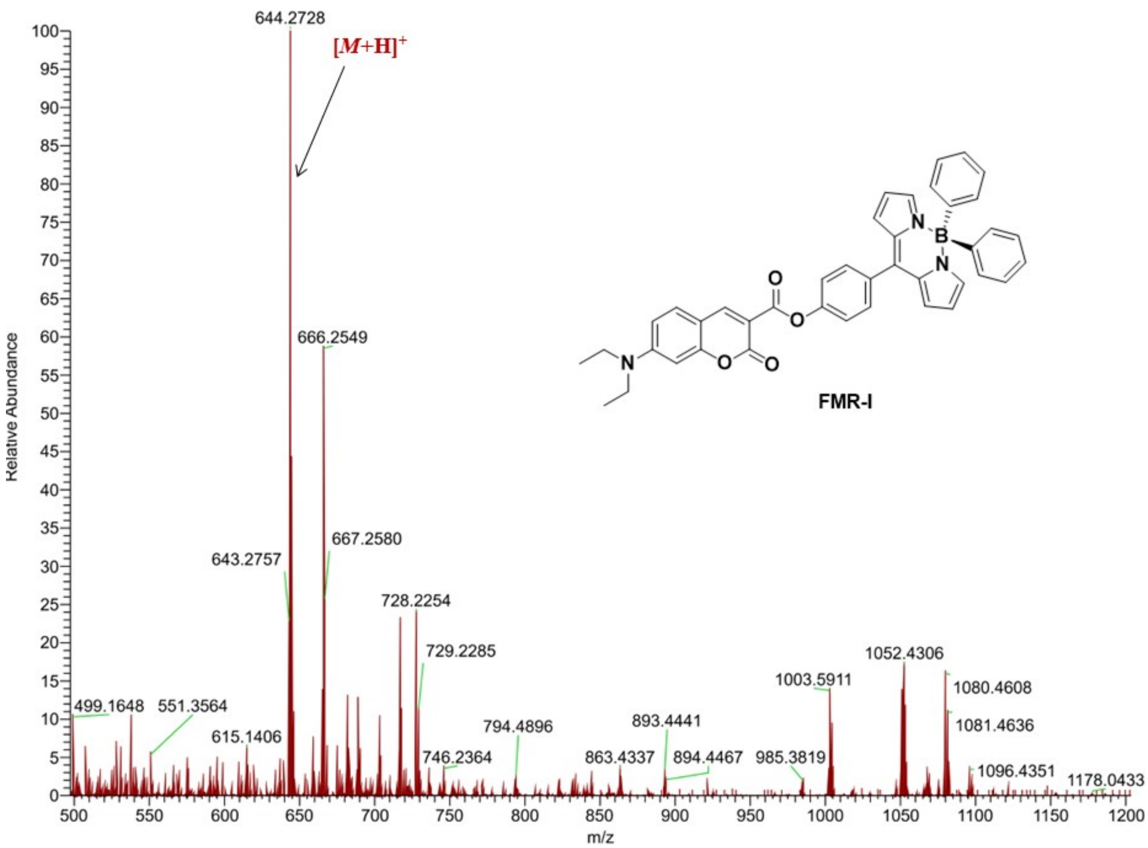


Figure S9. **HRMS** (ESI-TOF$^+$) spectrum for **FMR-I**.

Fluorescent Molecular Rotor II **(FMR-II)**.

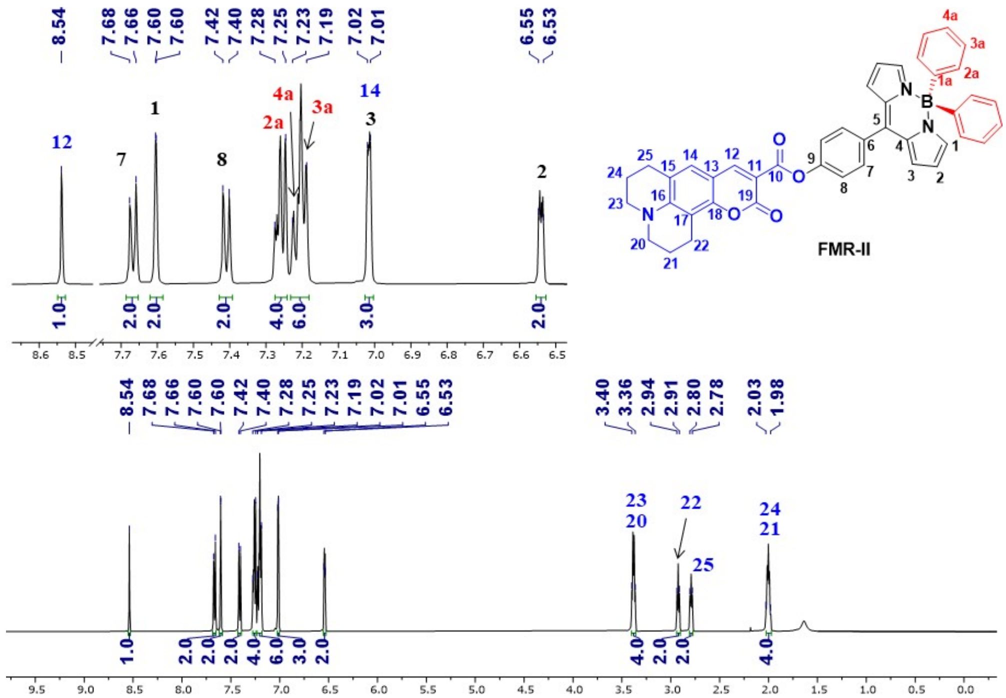


Figure S10. ^{1}H-NMR spectrum for **FMR-II** ($CDCl_3$, 500 MHz).

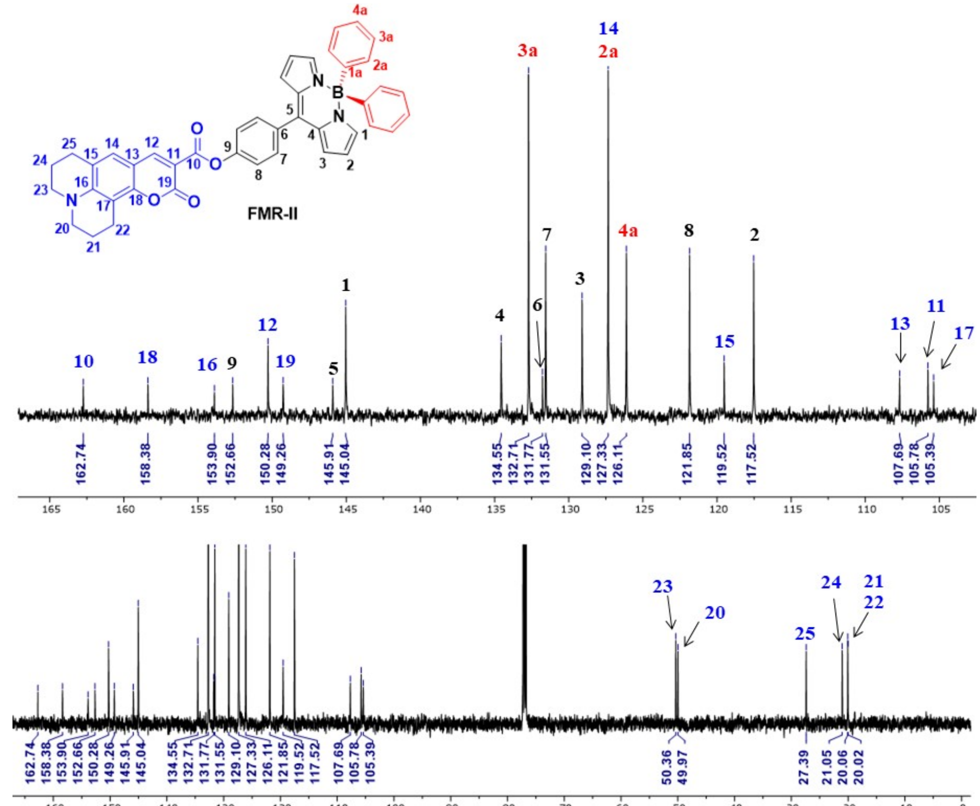


Figure S11. ^{13}C-NMR spectrum for **FMR-II** ($CDCl_3$, 125 MHz).

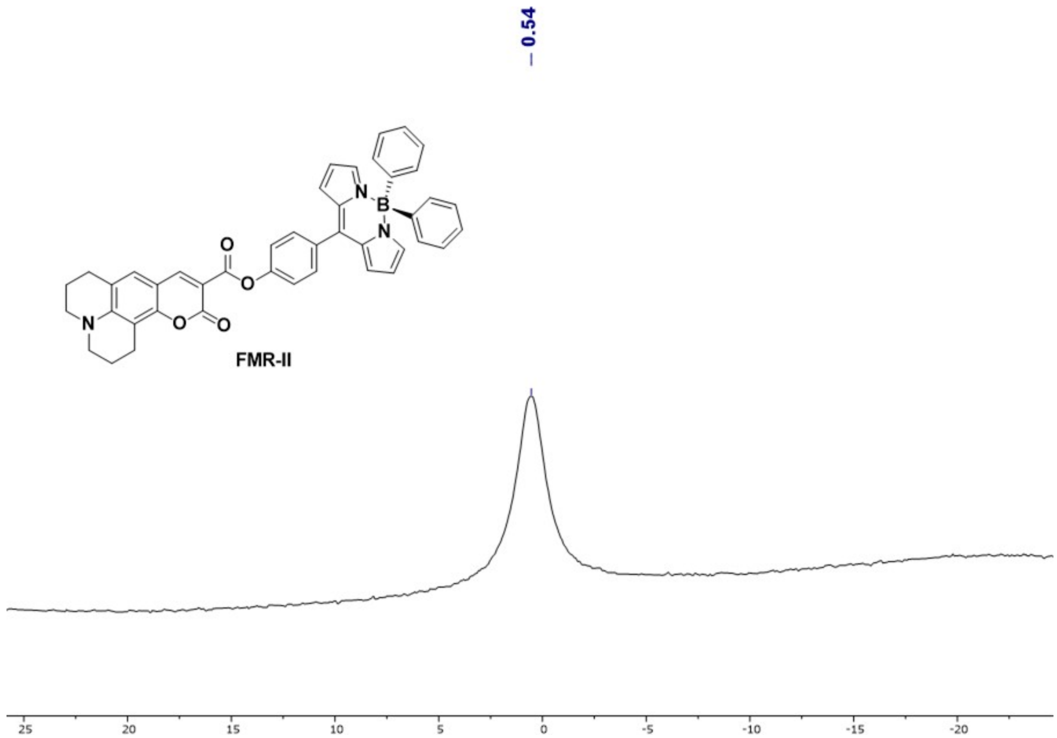


Figure S12. ^{11}B-NMR spectrum for **FMR-II** ($CDCl_3$, 128 MHz).

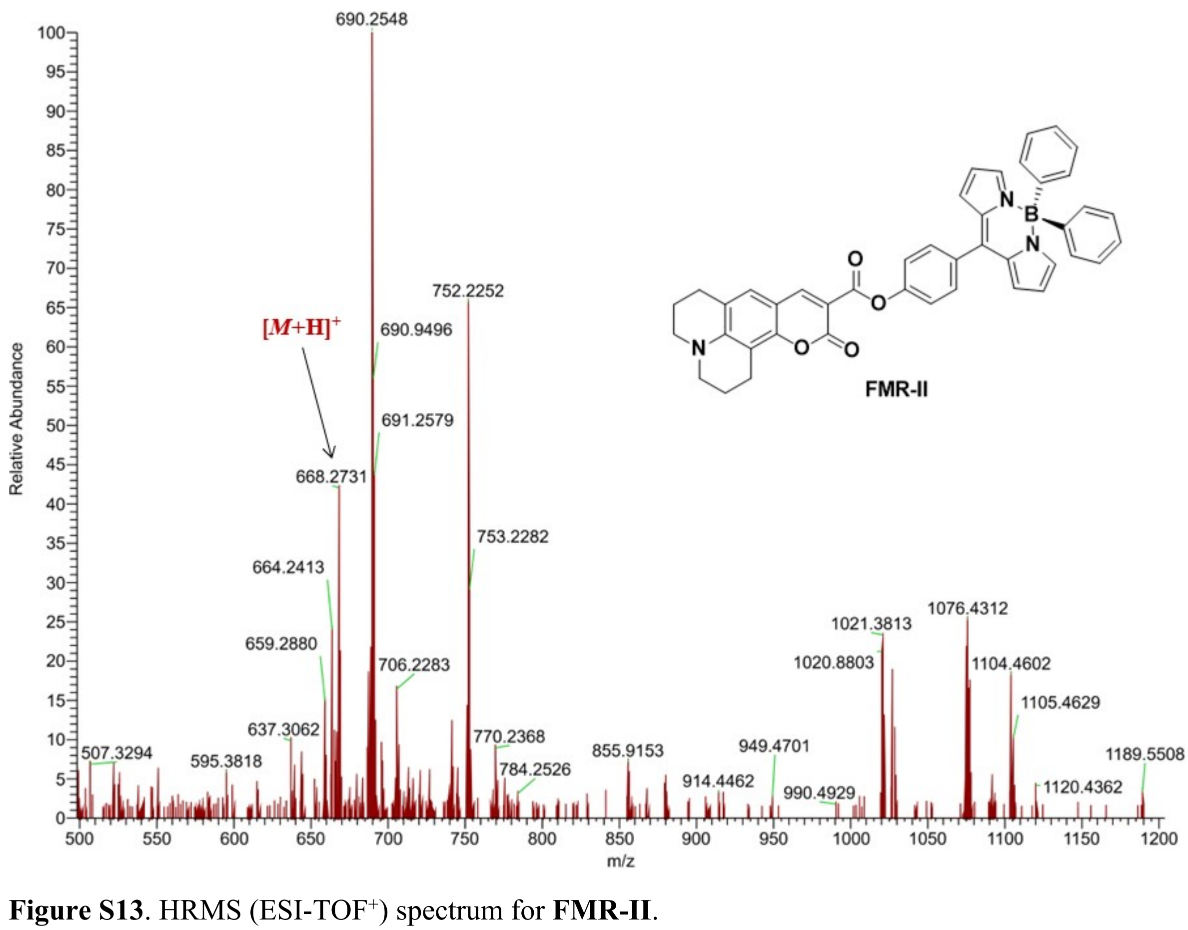


Figure S13. HRMS (ESI-TOF^{+}) spectrum for **FMR-II**.

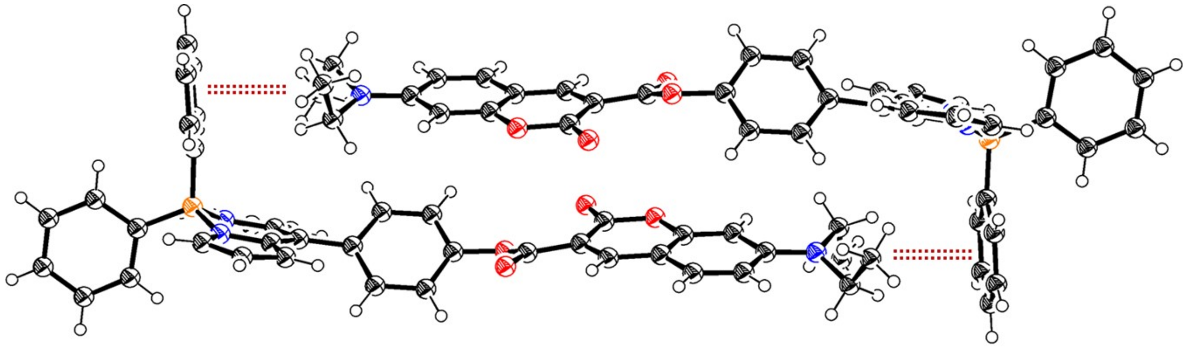
S3. Crystallography

Table S1. Crystal Structure and Refinement Data

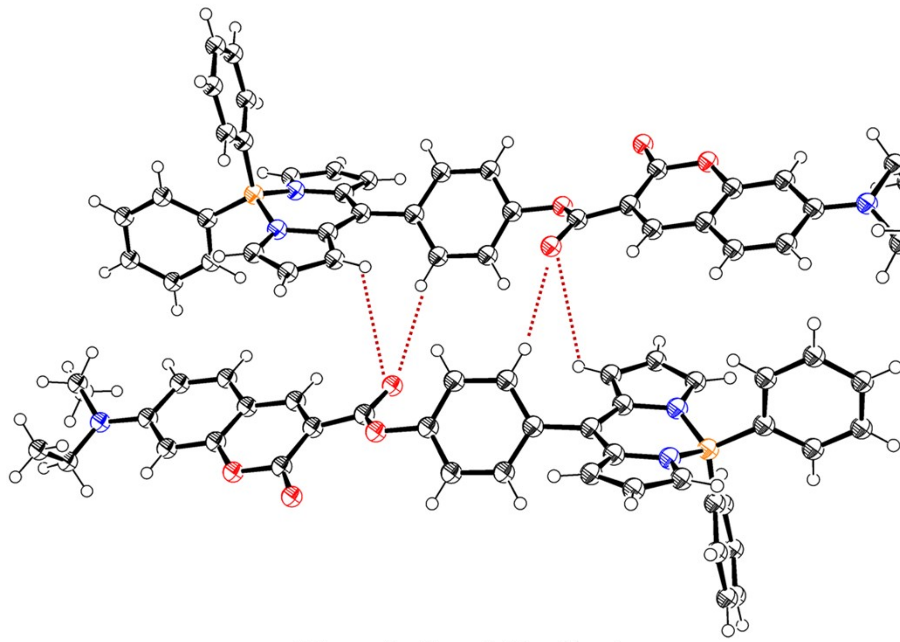
	FMR-I
Formula	$C_{41}H_{34}B_1N_3O_4$
M (g.mol^{-1})	643.52
Temperature (K)	293.13
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	8.6610(4)
b (Å)	12.4336(5)
c (Å)	16.0310(7)
α (deg)	103.570(2)
β (deg)	90.700(2)
γ (deg)	100.420(2)
volume (Å^3)	1647.77(13)
Z	2
Density (g·cm^{-3})	1.297
μ (mm^{-1})	0.084
Crystal size (mm)	0.21x0.19x0.08
Reflns collected/unique (Rint)	20278/4231 (0.0579)
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0417$
	$wR_2 = 0.0968$
R indices (all data)	$R_1 = 0.0625$
	$wR_2 = 0.1077$

$R = \Sigma||F_o| - |F_c||/ \Sigma |F_o|$. $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$.

The crystal packing of **FMR-I** is dominated by the formation of dimeric structures of the fluorophore, illustrated in Figure S14. In the first type of dimer (Dimer 1), the two fluorophore units are related to each other by inversion symmetry and closely stacked with an intercentroid distance of 4.291 Å between neighboring lactoid rings (C17-C18-C19-C24-O4-C25). Because the dipole moment of the fluorophores are oriented from the electron-rich coumarine towards the electron-withdrawing BODIPY fragment, the symmetrical face-to-face arrangement in Dimer 1 leads to a vanishing dipole moment. Both this electrostatic effect and the concomitant occurrence of C-H···π contacts between the diethylamino group and the phenyl ring of an adjacent BPh_2 moiety, result in a significant stabilizing interaction energy (E_{int}) for Dimer 1 of -32 kcal/mol, estimated as the energy difference between the dimer and the energy of two independent monomers, from values obtained by DFT computations on structurally-relaxed geometries at the M06-2X/6-31+G(d,p) level of theory in vacuum. In Dimer II, the fluorophores are related to each other by two-fold rotational symmetry forming an assembly held together through C3-H3···O2 and C11-H11···O2 contacts. Due to large H···O distances (above 3 Å) and poor directionalities, these supramolecular contacts can be regarded as weak and rather electrostatic non-classical hydrogen bonding interactions,[1, 2] leading to a lower E_{int} value for this assembly (E_{int} = -15 kcal/mol).



Dimer 1. E_{int} = -32 kcal/mol



Dimer 2. E_{int} = 15 kcal/mol

Figure S14. Crystallographic projections for dimeric interactions observed for **FMR-I**. Interaction energies (E_{int}) are presented as estimated at the M06-2X/6-31+G(d,p) level of theory in vacuum, from structurally-relaxed conformations of the dimers, where H-atoms and heavier disordered atoms are allowed to optimize freely.

S4. Miscellaneous Data

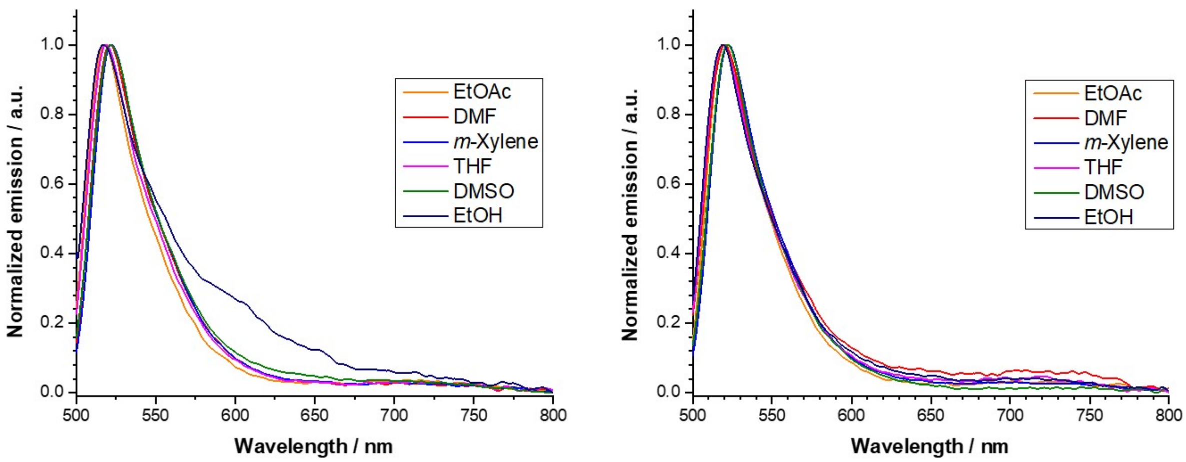


Figure S15. Fluorescence spectra for **FMR-I** and **FMR-II** in different solvents at 10^{-5} M under excitation at λ_{exc}=490 nm.

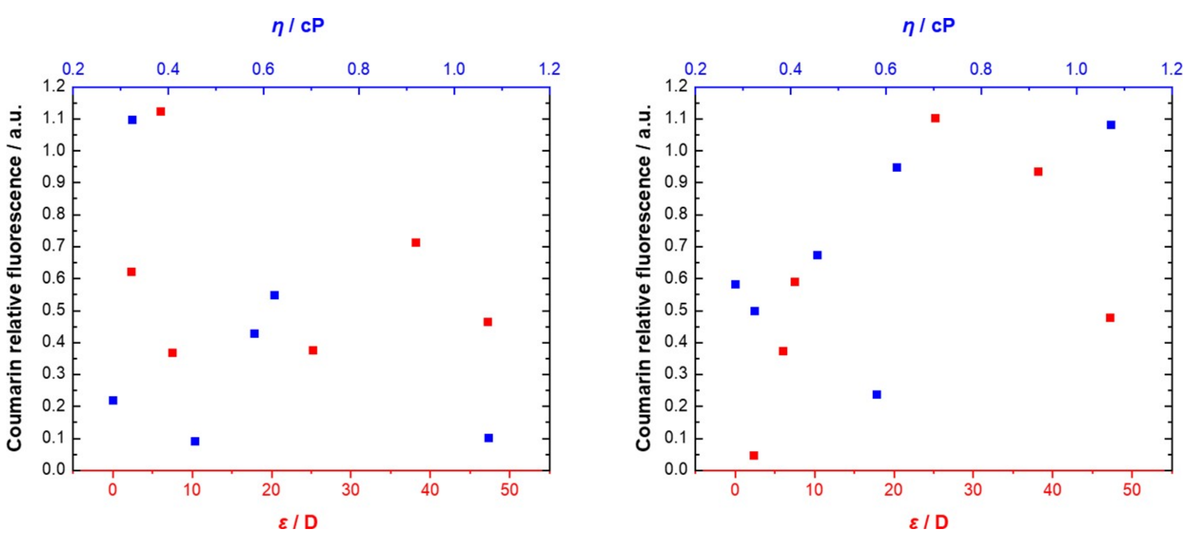


Figure S16. Plots of the relative fluorescence intensity of the coumarin band vs the dielectric constant (ε) and the viscosity (η) in different solvents for **FMR-I** (left) and **FMR-II** (right). The fluorescence intensity is normalized with respect to the corresponding emission of the BODIPY fluorophore.

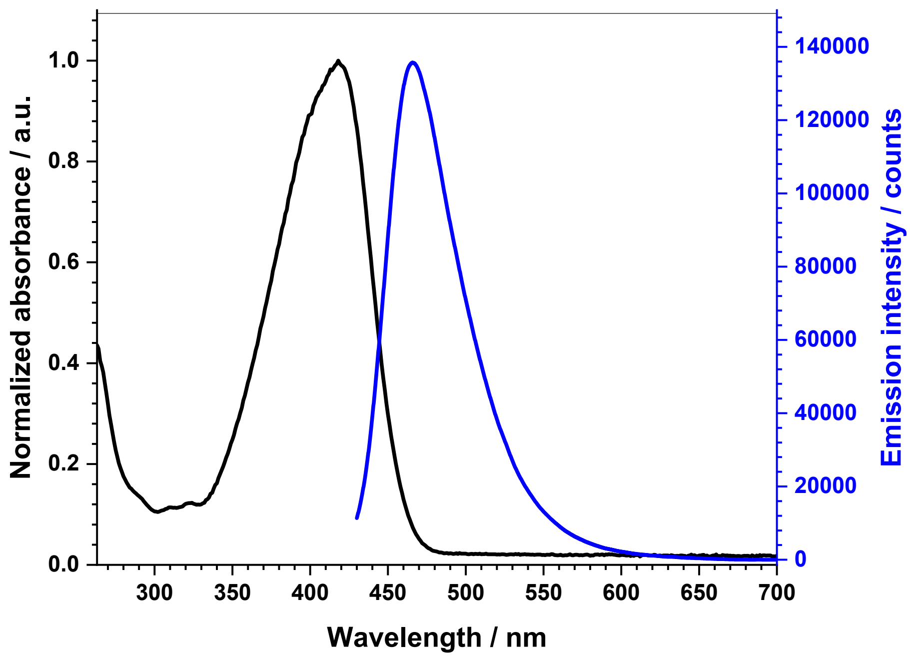


Figure S17. UV-Vis (black line) and emission (blue line, λ_{exc} = 420 nm) spectra for **3a** in DMSO (10^{-5} M).

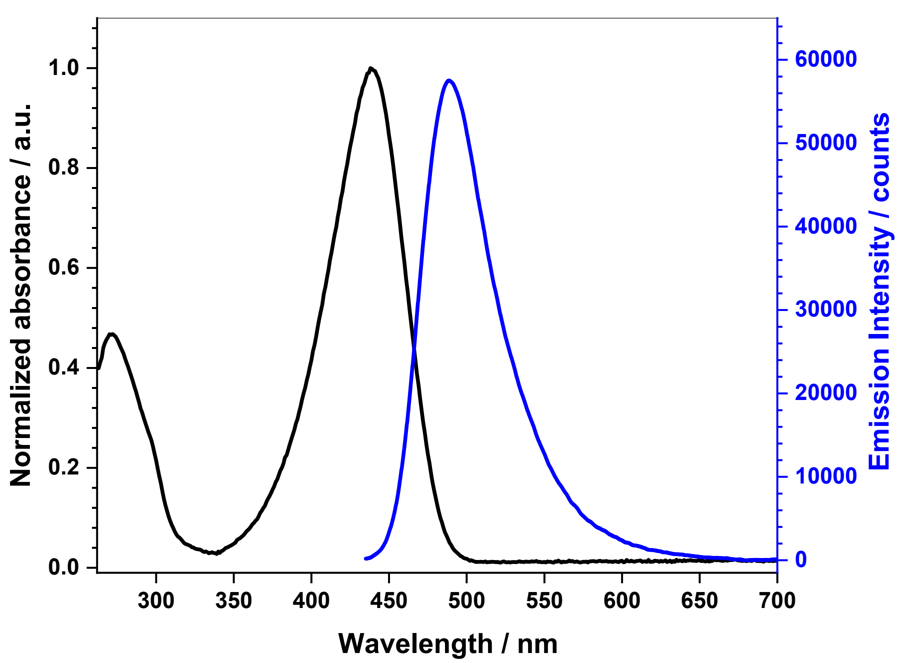


Figure S18. UV-Vis (black line) and emission (blue line, λ_{exc} = 440 nm) spectra for **3b** in DMSO (10^{-5} M).

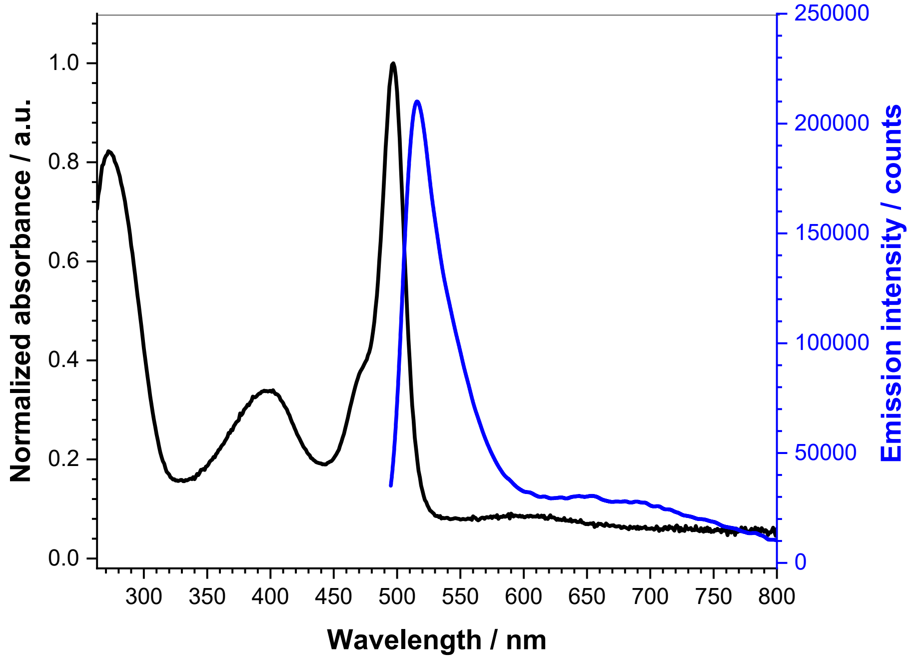


Figure S19. UV-Vis (black line) and emission (blue line, λ_{exc} = 490 nm) spectra for BODIPY **2** in DMSO (10^{-5} M).

Table S2. Photophysical data for compounds **3a-b** and BODIPY **2** in DMSO **(**10^{-5} M)

	λ_{max} / nm (ε / $M^{-1}cm^{-1}$)	Φ_F
3a	418 (44000)	0.0981
3b	438 (73000)	0.737
BODIPY 2	497 (81000)	$4x10^{-4}$

S5. References

1. C. M. Ramírez-Lozano, M. Eugenia Ochoa, P. Labra-Vázquez, N. Farfán and R. Santillan, *J. Mol. Struct.*, 2023, **1272**, 134191.
2. T. Steiner, *Crystallogr. Rev.*, 1996, **6**, 1-51.