A Non-Templated Approach for Tuning the Spectral Properties of cyanine-based Fluorescent NanoGUMBOS

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SUPPORTING INFORMATION

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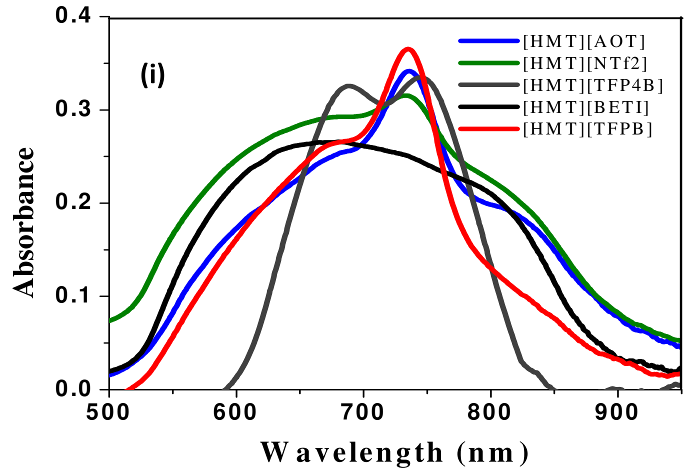
Table S1. Elemental analysis of HMT GUMBOS

NIR GUMBOS	C		H		N	
	Theory	**Found**	**Theory**	**Found**	**Theory**	**Found**
[HMT][AOT]	70.82	69.38	8.49	8.63	3.37	3.35
[HMT][NTf$_2$]	53.98	53.99	4.82	4.79	6.09	6.19
[HMT][TFPB]	64.31	61.97	5.21	4.92	4.05	3.61
[HMT][BETI]	50.72	50.19	4.19	4.21	5.34	5.32
[HMT][TFP4B]	47.02	50.91	3.18	4.66	1.29	0.84



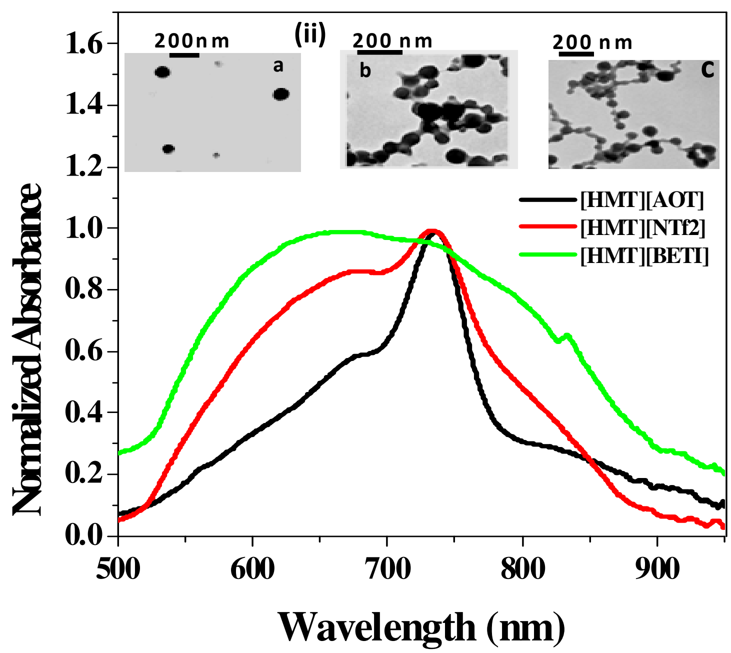


Figure S1. (i) Normalized absorption spectra of HMT nanoGUMBOS (ii)Normalized absorption spectra of same sized (~ 70 nm) HMT nanopartilces, insetTEM images of (a)[HMT][AOT], (b)[HMT][NTf$_2$] and (c)[HMT][BETI]

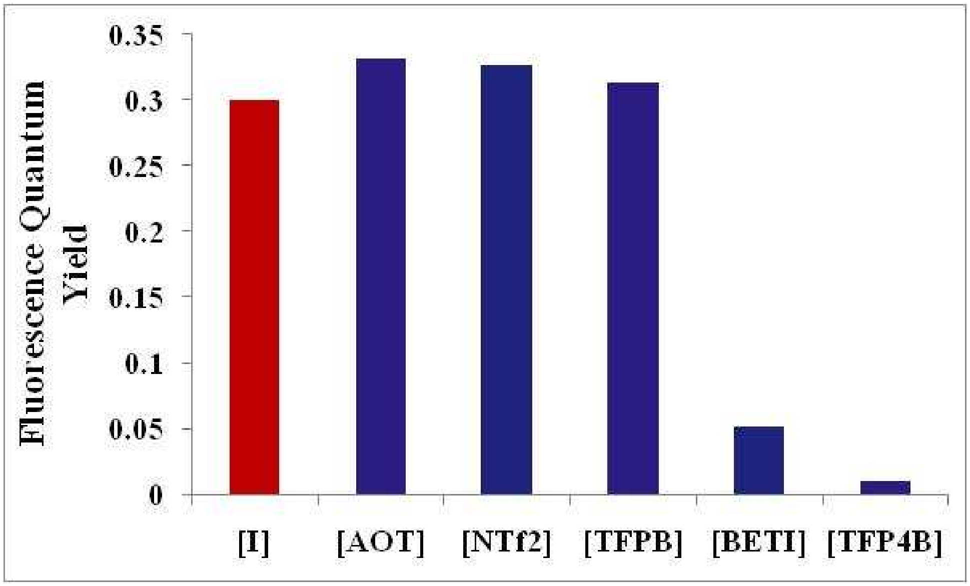


Figure S2. Fluorescence quantum yield of the HMT nanoGUMBOS (blue) and [HMT][I] (red) in Water Obtained with ICG as a standard.

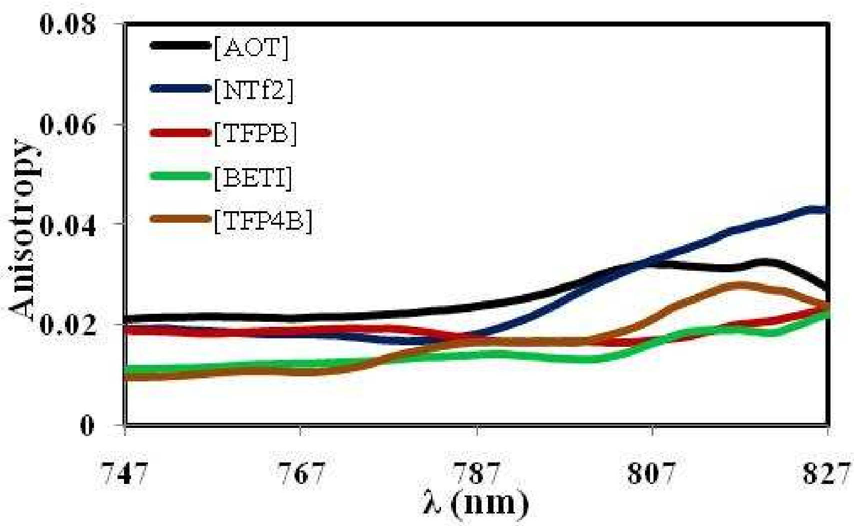


Figure S3. Fluorescence emission anisotropy of dilute ethanolic solutions of HMT anion pairs

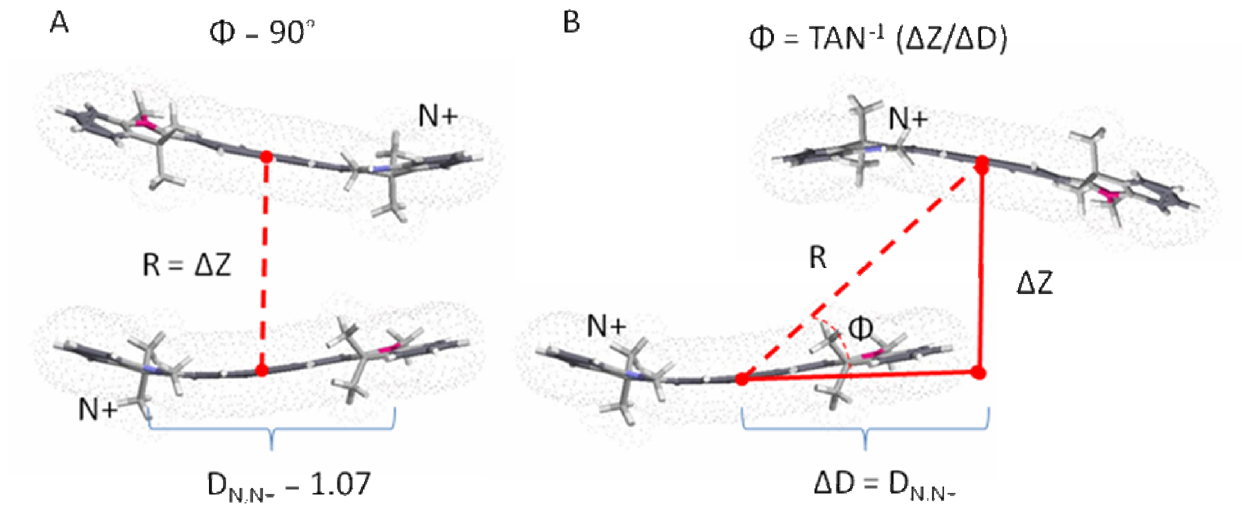


Figure S4. Postulated cation assemblies for a HMT H-aggregate (A) and a HMT J-aggregate (B). Stacking angle, Φ, depends on ΔZ and ΔD. A) HMT as a perfect H-aggregate, Φ = 90. B) HMT as a perfect J-aggregate, $\Phi_{tran} = TAN^{-1} (\Delta Z/D_{N,N+})$.

Characterization by ^{1}H NMR and ^{19}F NMR

[HMT][NTf$_2$], ^{1}H NMR (400 MHz, DMSO-d$_6$), δ (ppm): 7.84 (d, 1H), 7.55 (m, 1H), 7.39 (d, 1H), 7.37 (s, 1H), 7.35 (s, 1H), 7.34 (s, 1H), 7.24 (s, 1H), 7.22 (s, 1H), 7.20 (s, 1H), 7.08 (s, 1H), 7.06 (s, 1H), 6.52 (t, 1H), 6.07 (d, 1H) , 5.30 (s, 2H), 3.57 (s, 6H), 1.68 (s, 6H), 1.57 (s, 6H). ^{19}F NMR (236 MHz, DMSO-d$_6$), δ (ppm): -79.2

[HMT][BETI], ^{1}H NMR (400 MHz, DMSO-d$_6$), δ (ppm): 7.83 (d, 1H), 7.56 (m, 1H), 7.39 (d, 1H), 7.37 (s, 1H), 7.35 (s, 1H), 7.34 (s, 1H), 7.24 (s, 1H), 7.21 (s, 1H), 7.20 (s, 1H), 7.08 (s, 1H), 7.06 (s, 1H), 6.52 (t, 1H), 6.07 (d, 1H) , 5.31 (s, 2H), 3.56 (s, 6H), 1.68 (s, 6H), 1.57 (s, 6H). ^{19}F NMR (236 MHz, DMSO-d$_6$), δ (ppm): -79.0, -79.2 .

[HMT][TFPB], ^{1}H NMR (400 MHz, DMSO-d$_6$), δ (ppm): 8.51 (s, 1H), 8.15 (s, 2H), 7.84 (d, 1H), 7.55 (m, 1H), 7.39 (d, 1H), 7.37 (s, 1H), 7.35 (s, 1H), 7.34 (s, 1H), 7.24 (s, 1H), 7.22 (s, 1H), 7.20 (s, 1H), 7.08 (s, 1H), 7.06 (s, 1H), 6.52 (t, 1H), 6.07 (d, 1H) , 5.30 (s, 2H), 3.57 (s, 6H), 1.68 (s, 6H), 1.57 (s, 6H). ^{19}F NMR (236 MHz, DMSO-d$_6$), δ (ppm): -62.7, -63.0, -63.1.

[HMT][TFP4B], ^{1}H NMR (400 MHz, DMSO-d$_6$), δ (ppm): 7.84 (d, 1H), 7.55 (m, 1H), 7.50 (s, 4H), 7.39 (d, 1H), 7.37 (s, 1H), 7.35 (s, 1H), 7.34 (s, 1H), 7.26 (s, 8H), 7.24 (s, 1H), 7.22 (s, 1H), 7.20 (s, 1H), 7.08 (s, 1H), 7.06 (s, 1H), 6.52 (t, 1H), 6.07 (d, 1H) , 5.30 (s, 2H), 3.57 (s, 6H), 3.25 (s, 24H), 1.68 (s, 6H), 1.57 (s, 6H). ^{19}F NMR (236 MHz, DMSO-d$_6$), δ (ppm): -71.8.

[HMT][AOT], ^{1}H NMR (400 MHz, DMSO-d$_6$), δ (ppm): 7.82 (d, 1H), 7.55 (m, 1H), 7.38 (d, 1H), 7.37 (s, 1H), 7.35 (s, 1H), 7.34 (s, 1H), 7.24 (s, 1H), 7.22 (s, 1H), 7.20 (s, 1H), 7.08 (s, 1H), 7.06 (s, 1H), 6.52 (t, 1H), 6.07 (d, 1H) , 5.30 (s, 2H), 6.23 (t, 1H), 4.24 (d, 4H), 4.95 (d, 2H), 2.35 (m, 2H), 3.57 (s, 6H), 1.68 (s, 6H), 1.57 (s, 6H), 1.54 (m, 4H), 1.25 (m, 10H), 0.84 (t, 12H).

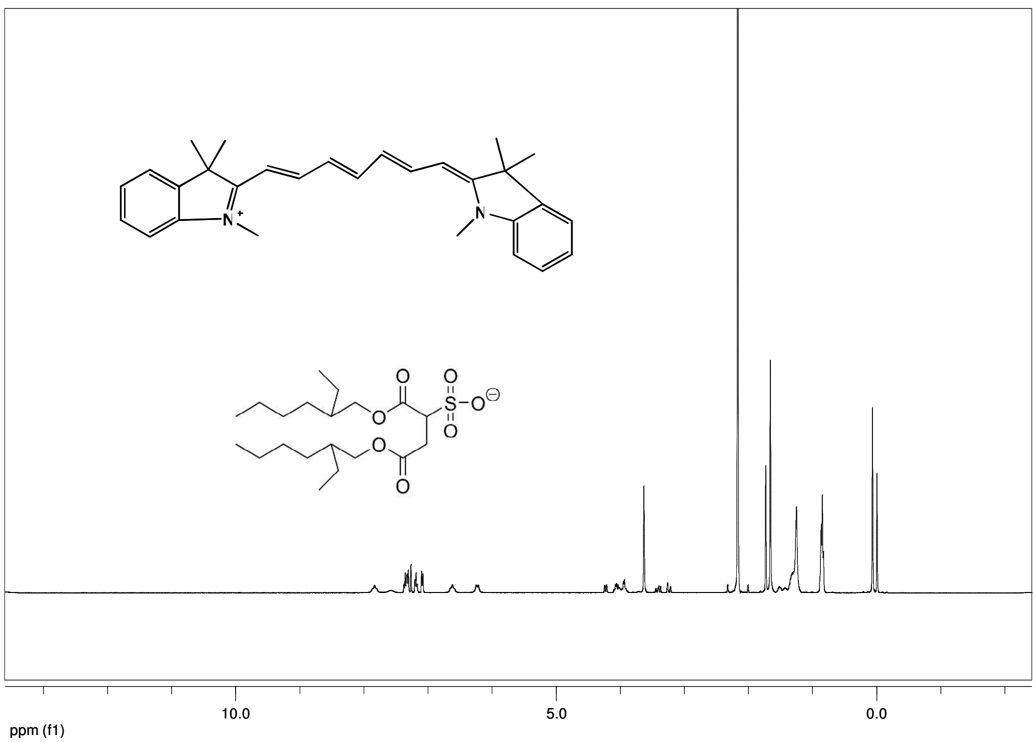


Figure S5-1. ^{1}H NMR (CDCl$_3$, 400MHz) of [HMT][AOT].

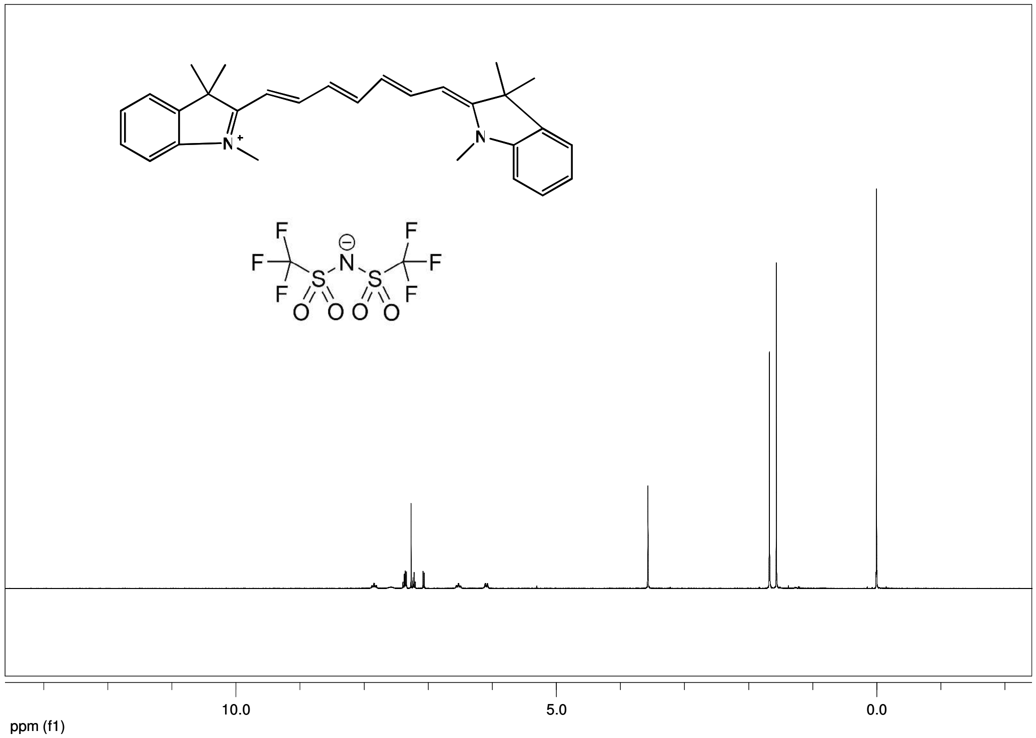


Figure S5-2a. ^{1}H NMR ($CDCl_3$, 400MHz) of [HMT][NTf_2].

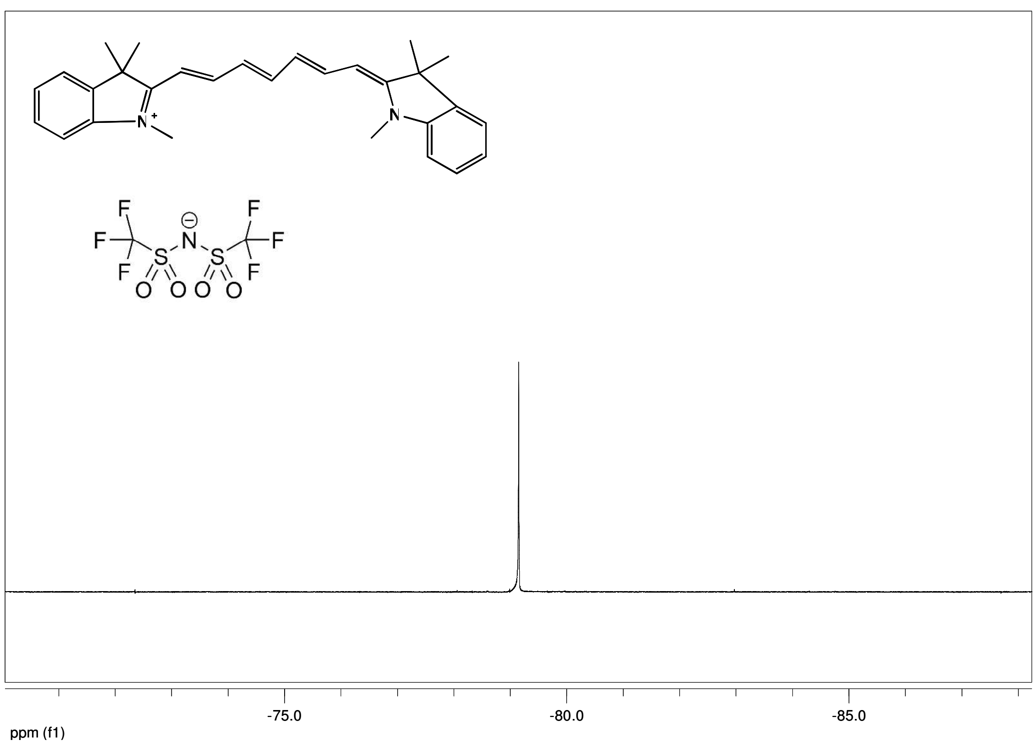


Figure S5-2b. ^{19}F NMR ($CDCl_3$, 236MHz) of [HMT][NTf_2]

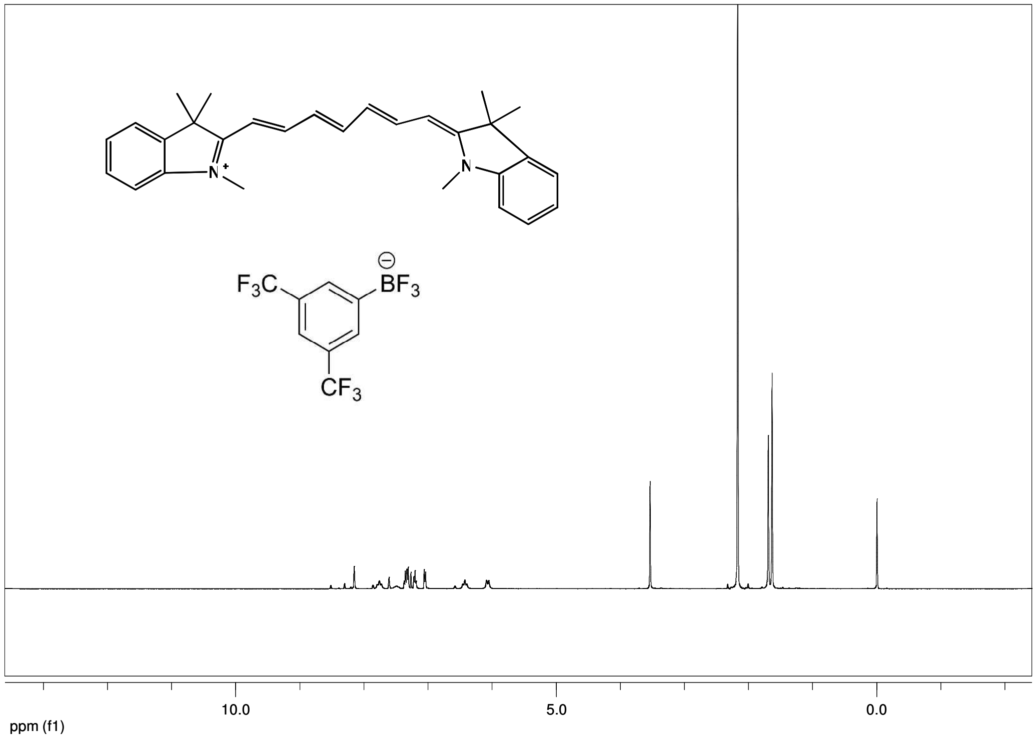


Figure S5-3a. ^{1}H NMR ($CDCl_3$, 400MHz) of [HMT]TFPB]

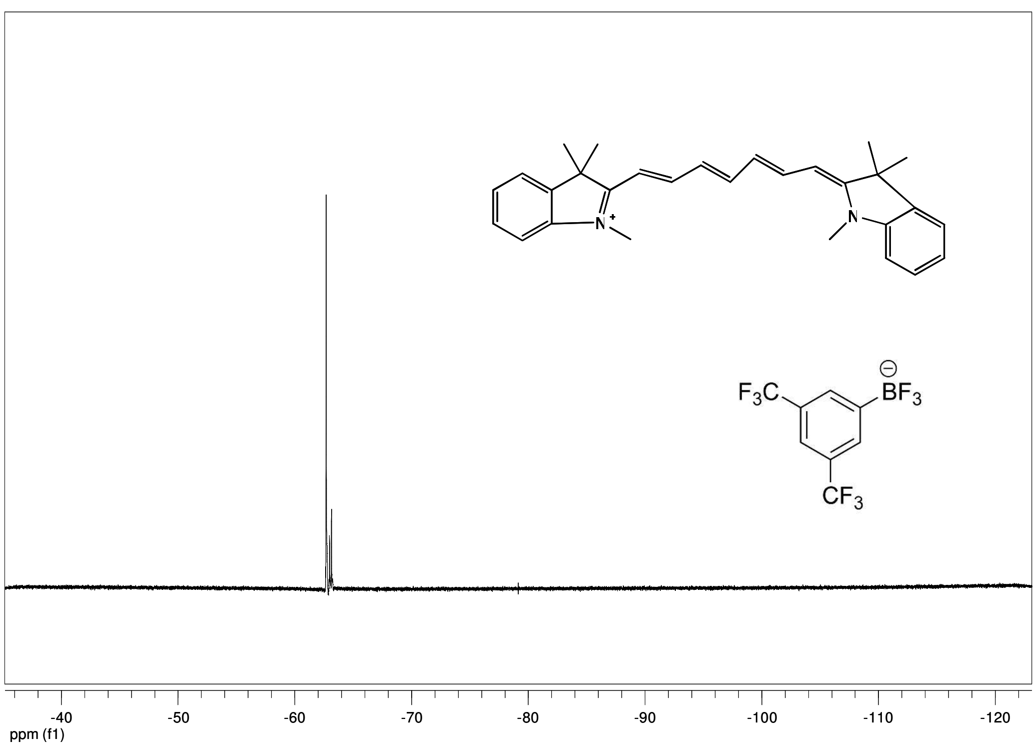


Figure S5-3b. ^{19}F NMR ($CDCl_3$, 236MHz) of [HMT][TFPB].

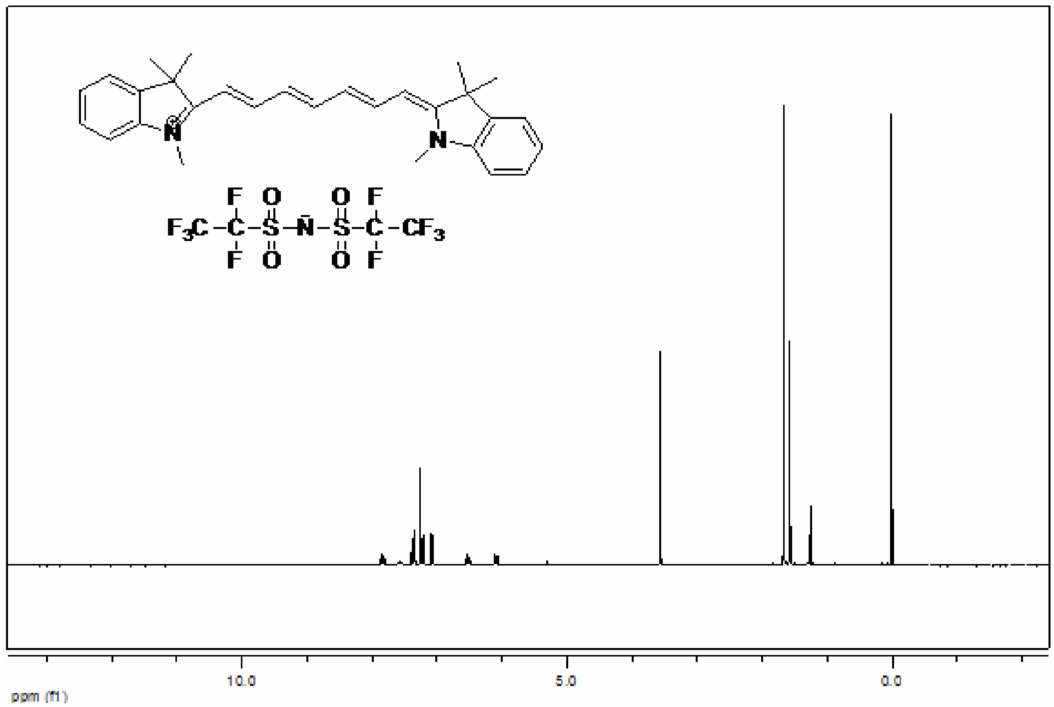


Figure S5-4a. 1H NMR ($CDCl_3$, 400MHz) of [HMT][BETI]

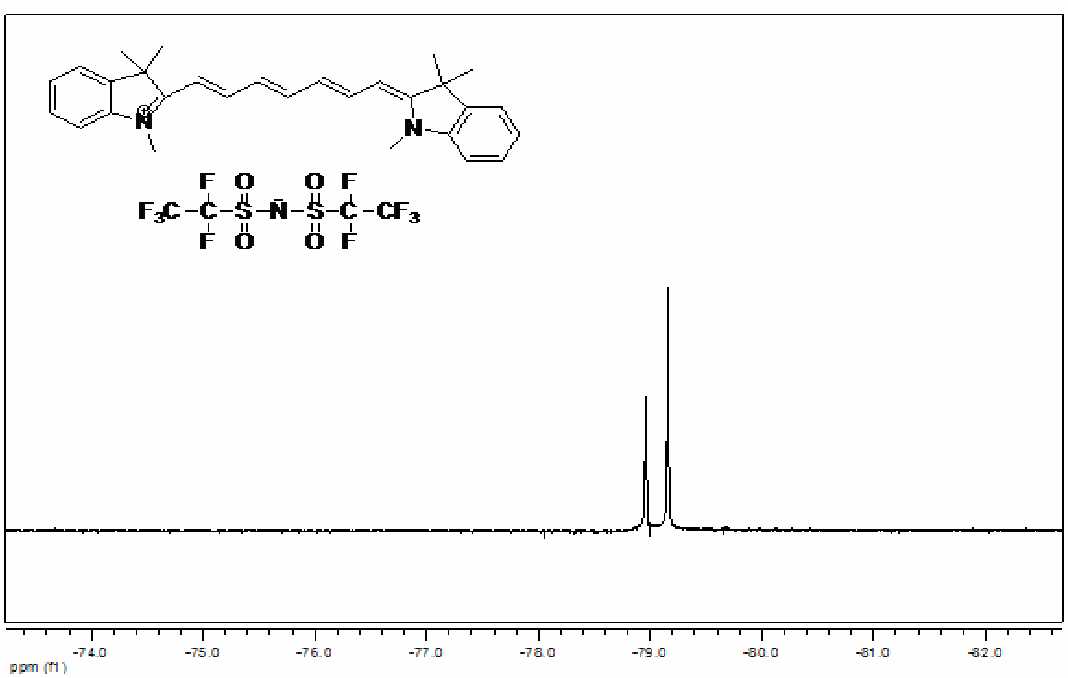


Figure S5-4b. ^{19}F NMR ($CDCl_3$, 236MHz) of [HMT][BETI]

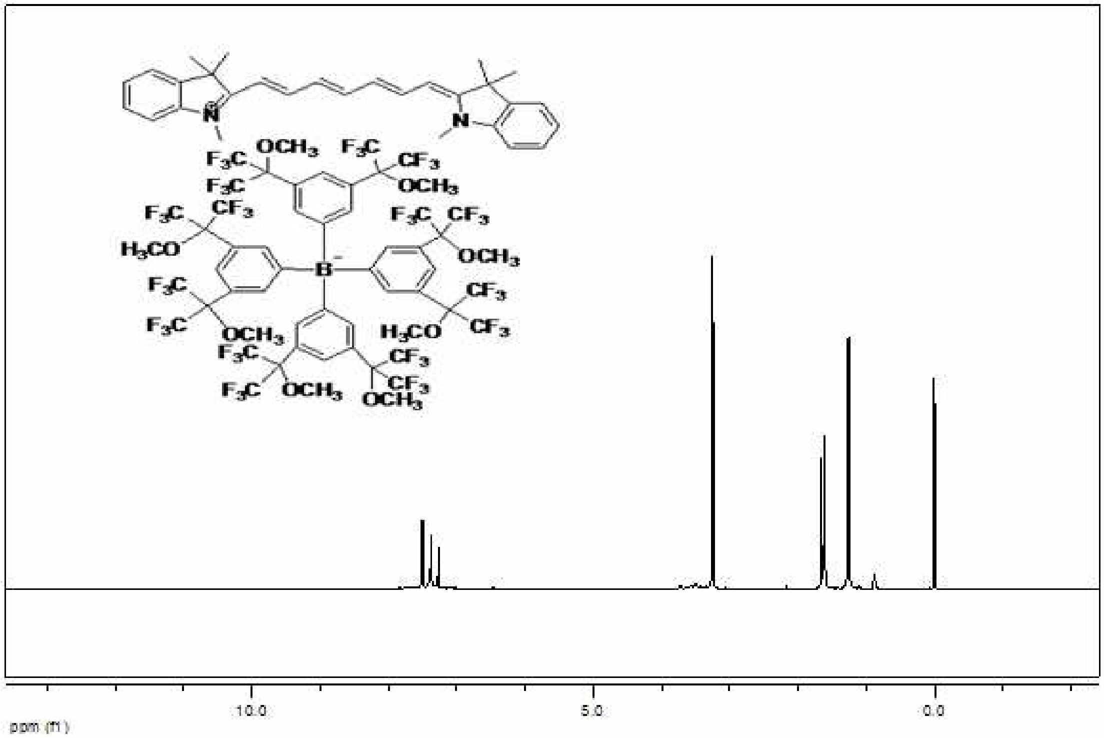


Figure S5-5a. ^{1}H NMR ($CDCl_3$, 400MHz) of [HMT][TFP4B]

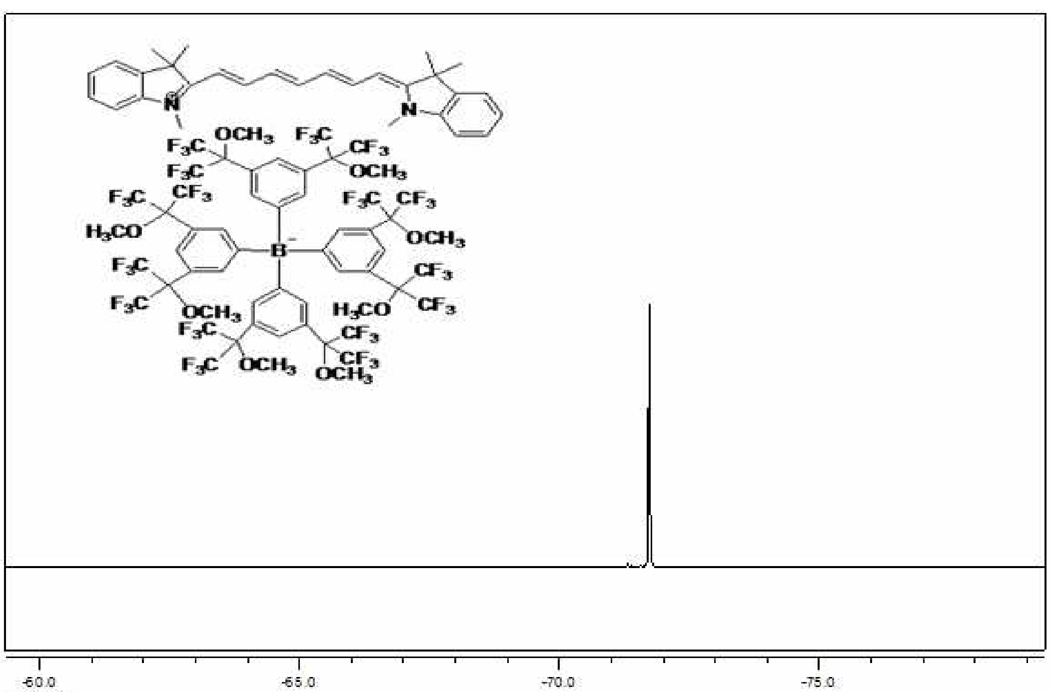


Figure S5-5b. ^{19}F NMR ($CDCl_3$, 236MHz) of [HMT][TFP4B]