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Supplementary material

SUPPLEMENTARY MATERIAL TO

New pyrene and fluorene-based π-conjugated Schiff bases: Theoretical and experimental investigation of optical properties

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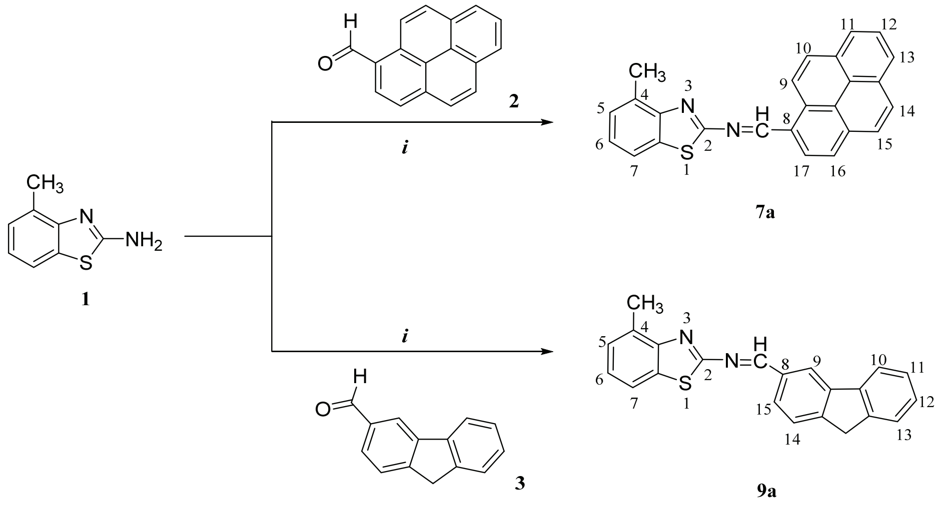
EXPERIMENTAL



i: EtOH, 75 °C, reflux, %5 HCl, N_2(g)

Scheme S-1**.** Synthesis method and numbers of protons.

SPECTROSCOPIC DATA OF MAIN COMPOUNDS

N-(pyren-1-ylmethylene)-4-methylbenzo[d]thiazol-2-amine (7a) Yield: 50 %, mp. 212-216 °C. FT-IR (KBr, cm^{-1}): 3038 (Aromatic C-H), 2965-2918 (Aliphatic C-H), 1593 (CH=N),

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–1576, 1537 and 1478 (C=C) (Fig.S1). ^{1}H NMR (500 MHz, DMSO-d_6, δ ppm): 9.98 (s, 1H, CH=N), 9.28 (d, 1H, J=9 Hz, H17), 8.84 (d, 1H, J= 7 Hz, H10), 8.44 (m, 5H, H9, H11, H14, H15, H16), 8.28 (d, 1H, J= 8.9 Hz, H13), 8.15 (t, 1H, J= 8.6 Hz, H12), 7.88 (dd, 1H, H6), 7.31 (d, 2H, H5 ve H7), 2.45 (s, 3H) (Fig.S2). ^{13}C NMR (125 MHz, DMSO-d_6, δ ppm): 135.0 (CH=N), 134.36, 132.80, 131.74, 131.21, 130.86, 130.61, 130.53, 129.08, 127.09, 127.67, 127.59, 127.50, 127.41, 125.83, 124.51, 123.93, 123.28, 120.25. ESI-MS (m/z): 377.68 (M^+), 378.71 (M^++1), 379.77 (M^++2), 245.48 (M^+ -$C_8H_8N_2S$), 165.15 (M^+ -$C_{17}H_{19}$). Anal. Calcd. for $C_{25}H_{16}N_2S$: C, 79.76; H, 4.28; N, 7.44; S, 8.52. Found: C, 79.52; H, 4.44; N, 7.37; S, 8.40.

N-(9H-fluoren-3-ylmethylene)-4-methylbenzo[d]thiazol-2-amine (9a) Yield: 60 %, mp. 180-183 °C. FT-IR (KBr, cm^{-1}): 3046 (Aromatic C-H), 2957, 2910 (Aliphatic C-H), 1620 (CH=N), 1586, 1549 and 1518 (C=C) (Fig.S3). ^{1}H NMR (500 MHz, DMSO-d_6, δ ppm): 9.14 (s, 1H, -CH=N-), 8.26 (s, 1H, H9), 8.07 (d, 2H, J=1.5 Hz H14 and H15), 7.99 (d, 1H, J= 7.0 Hz, H7), 7.80 (dd, 1H, J=2.5 Hz, J=8 Hz, H10), 7.62 (d, 1H, J=8.0 Hz, H5), 7.39 (t, 1H, J=7.5 Hz, H6 and dt, 1H, J=8 Hz, H12), 7. 28 (d, 1H, J=8.0 Hz, H13 and t, 1H J=7 Hz, H11), 4.00 (s, 2H, Fluorene –CH_2), 2.60 (s, 3H, -CH_3) (Fig.S4). ESI-MS (m/z): 341.63 (M^+), 342.63 (M^++1), 343.65 (M^++2), 209 (M^+ -$C_7H_5N_2S$), 165.1 (M^+ -fluorine). Anal. Calcd. for $C_{22}H_{16}N_2S$: C, 77.62; H, 4.74; N, 8.23; S, 9.42. Found: C, 79.90; H, 4.98; N, 8.23; S, 9.40.

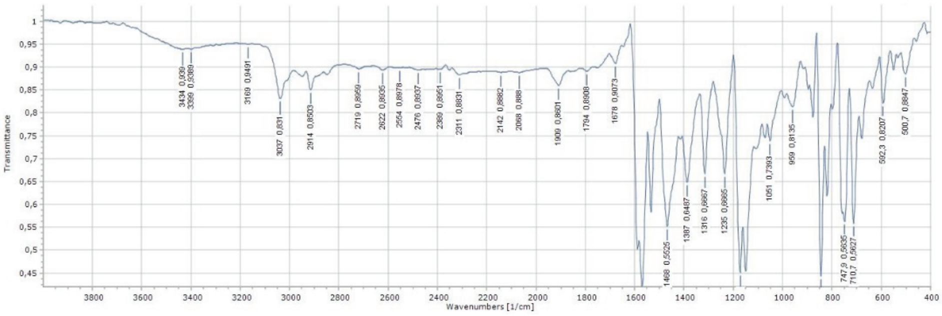

Fig. S-1. FT-IR spectrum of **7a**.

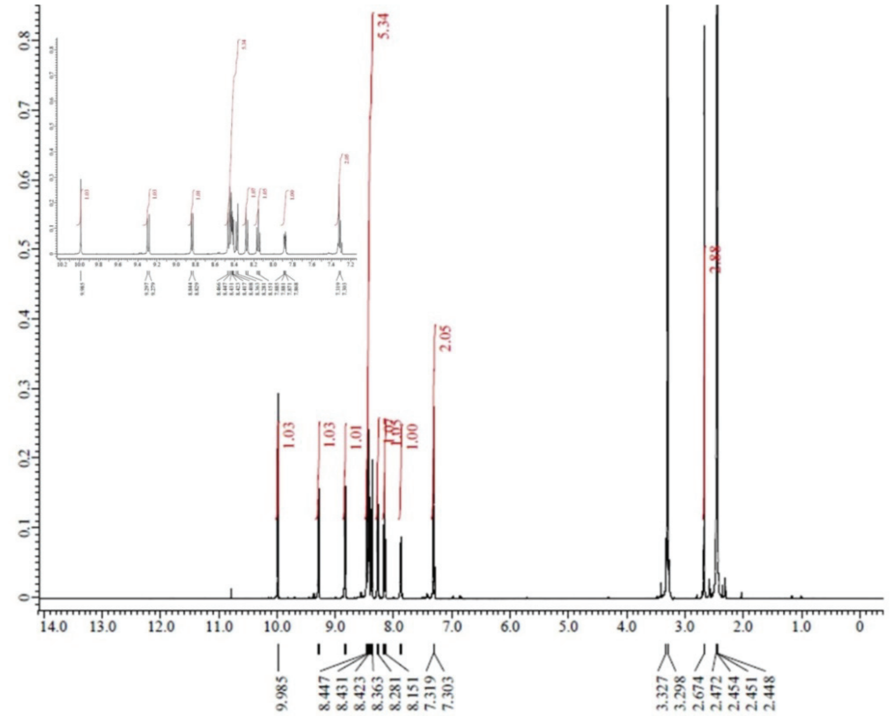

Fig. S-2. ^{1}H NMR spectrum of compound **7a**.

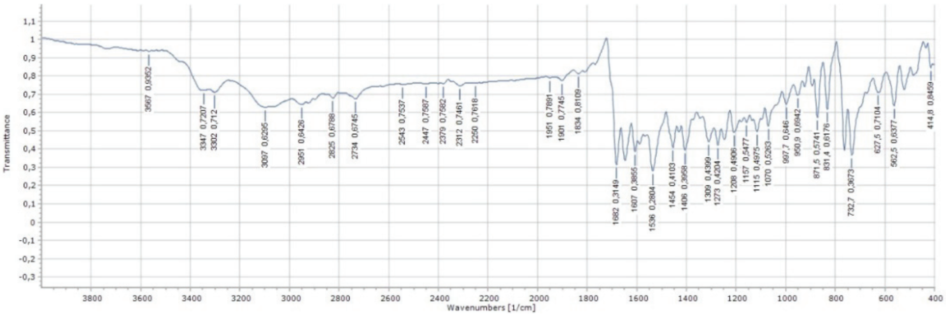

Fig. S-3. FT-IR spectrum of **9a**.

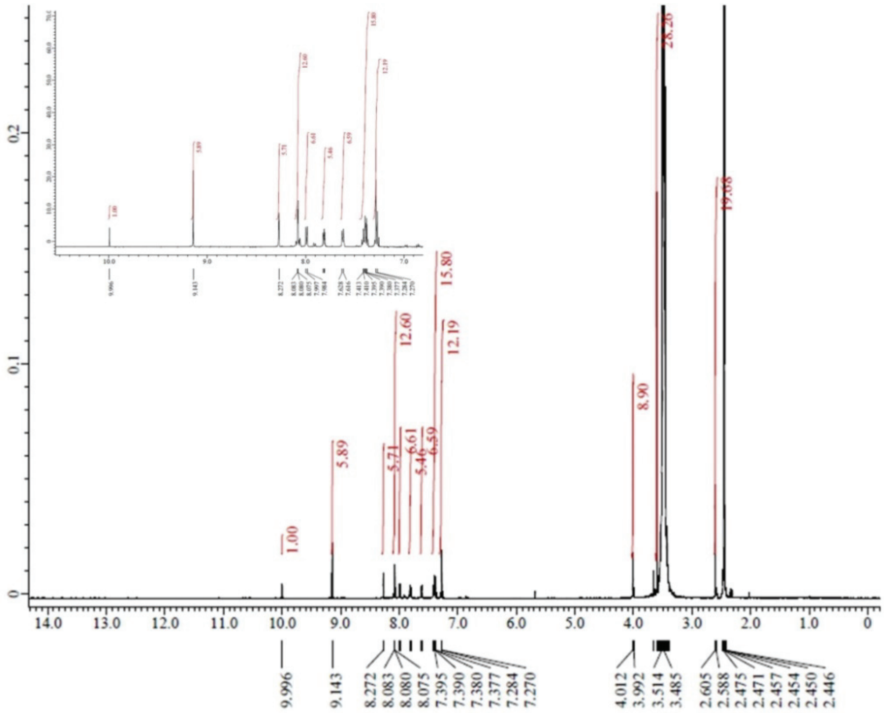

Fig. S-4. ^{1}H NMR spectrum of compound **9a**.

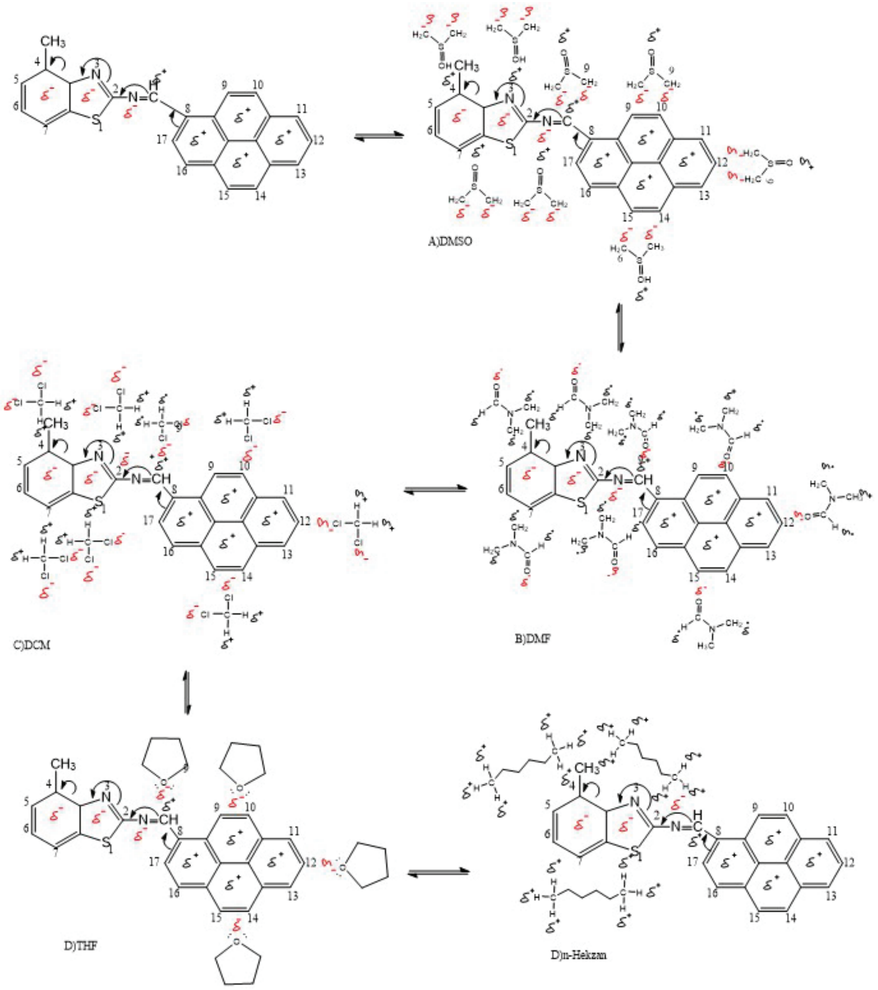

Fig. S-5. Resonance structures in different solvents for compound **7a**.

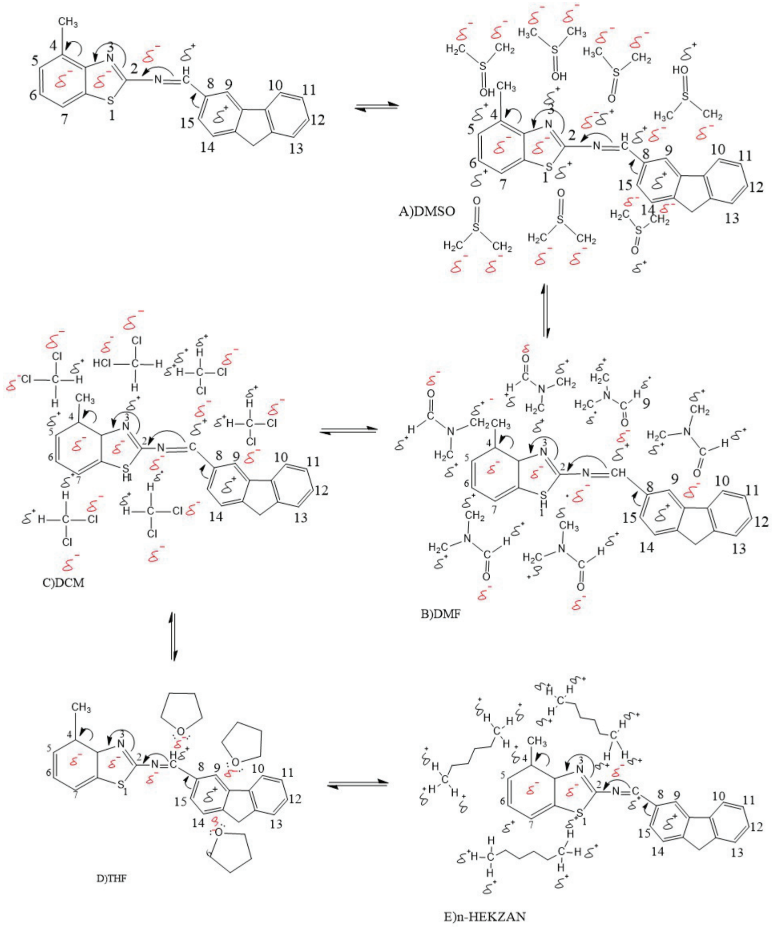

Fig. S-6. Resonance structures in different solvents for compound **9a**.

COMPUTATIONAL STUDY

Optimized Geometries

7a

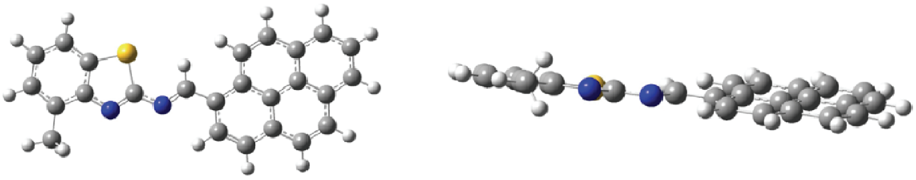

Fig. S-7. Front (left) and side (right) view of the optimized structure of compound **7a**.

Sum of electronic and thermal Free Energies (Hartree)= -1469.786060
Thermal correction to Gibbs Free Energy (Hartree)= 0.287006

C	-5.7557	-4.0026	0.0403
C	-4.8025	-4.9499	0.0676
C	-3.5033	-4.6125	0.1156
C	-3.1932	-3.3093	0.1353
C	-4.1457	-2.3685	0.108
C	-5.4488	-2.6917	0.0598
S	-1.8702	-2.6883	0.1863
C	-2.3634	-1.2992	0.1789
N	-3.6308	-1.2171	0.1341
N	-1.7306	-0.1971	0.2101
C	-0.4709	-0.0485	0.2569
C	-0.5637	2.2588	0.2734
C	-0.0138	3.4781	0.3045
C	1.319	3.6125	0.3545
C	2.0969	2.5118	0.3727
C	1.5341	1.2785	0.3408
C	0.1837	1.1368	0.2906
C	3.4378	2.6806	0.4232
C	4.2568	1.6119	0.4431
C	3.7152	0.3861	0.4118
C	2.3851	0.232	0.3617
C	3.9861	3.9133	0.4547
C	5.3219	4.0657	0.5046
C	6.1272	2.995	0.5239
C	5.5916	1.7674	0.4931
C	1.8605	4.8418	0.3857
C	3.1895	4.994	0.4357
C	-6.5436	-1.6528	0.0288
H	-6.8147	-4.3086	0.001
H	-5.089	-6.0151	0.0506
H	-2.7287	-5.3977	0.1378
H	0.1072	-0.9805	0.2704
H	-1.666	2.2343	0.2333
H	-0.6762	4.361	0.2885
H	4.3565	-0.5126	0.4267
H	2.0557	-0.8168	0.3395
H	5.7816	5.0685	0.5307
H	7.2219	3.123	0.5648
H	6.2682	0.8959	0.5096
H	1.2281	5.7462	0.371
H	3.607	6.0151	0.4605
H	-6.157	-0.6105	0.0607
H	-7.1454	-1.7565	-0.9027
H	-7.2219	-1.7825	0.9027

9a

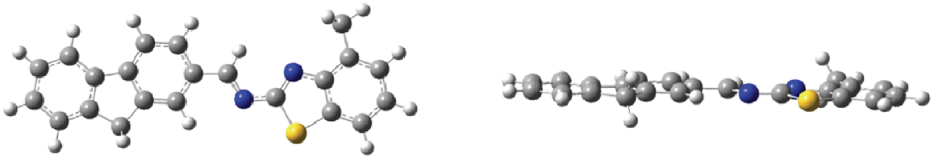

Fig. S-7. Front (left) and side (right) view of the optimized structure of compound **9a**.

Sum of electronic and thermal Free Energies (Hartree)=-1355.461210
Thermal correction to Gibbs Free Energy (Hartree)= 0.268929

C	7.0316	0.69762	0.24052
C	7.26734	-0.65893	-0.0043
C	6.22069	-1.54738	-0.19256
C	4.91385	-1.06566	-0.13392
C	4.67582	0.30957	0.11157
C	5.73912	1.20826	0.30349
S	3.41762	-1.94978	-0.32722
C	2.5349	-0.41676	-0.07801
N	3.29832	0.64939	0.13484
N	1.12015	-0.39232	-0.05995
C	0.42027	0.68441	-0.25694
C	-1.04407	0.63639	-0.20738
C	-1.74033	-0.55218	0.06513
C	-3.12127	-0.51314	0.09489
C	-3.81911	0.69399	-0.14285
C	-3.13384	1.86797	-0.41156
C	-1.74169	1.82843	-0.44165
C	-4.09047	-1.63175	0.35997
C	-5.42491	-0.94853	0.25127
C	-5.25135	0.42454	-0.04592
C	-6.69227	-1.48005	0.39949
C	-7.79082	-0.62966	0.24879
C	-7.61911	0.71905	-0.04313
C	-6.34252	1.26387	-0.19443
C	5.49993	2.649	0.56448
H	7.88589	1.36978	0.38561
H	8.29958	-1.02318	-0.04675
H	6.41233	-2.60878	-0.38288
H	0.87647	1.6678	-0.4669
H	-1.2047	-1.49079	0.25044
H	-3.67581	2.80149	-0.59496
H	-1.18593	2.75032	-0.65236
H	-3.98584	-2.44856	-0.3778
H	-3.93785	-2.07827	1.35986
H	-6.83293	-2.54066	0.62927
H	-8.80209	-1.03412	0.36289
H	-8.49628	1.3647	-0.1563
H	-6.20451	2.3253	-0.42418
H	4.94652	3.11196	-0.26377
H	4.90548	2.78929	1.4775
H	6.43807	3.20643	0.68978

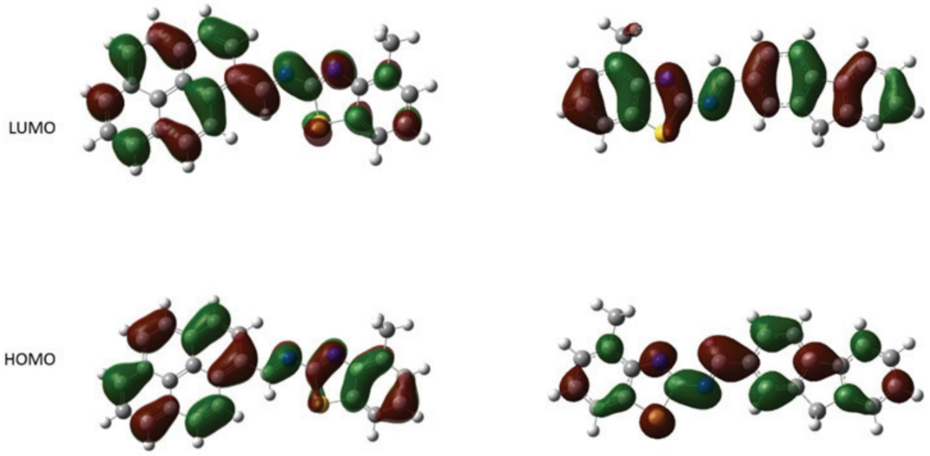

Fig. S-9. HOMOs and LUMOs of **7a** (left) and **9a** (right) estimated at the B3LYP/6-31G(d,p) level in the gas phase.

A dispersion component was added to the B3LYP 6-31 G (d,p) level of theory used in DFT calculations, and re-optimization and frequency calculations of the investigated 7a and 9a molecules were completed. The command line for frequency calculations with added dispersion component is given below:

```
freq=noraman b3lyp/6-31g(d,p) scrf=(cpcm,solvent=dmso) guess=save
geom=connectivity EmpiricalDispersion=GD3BJ
```

First, there is no difference in the dihedral angles and therefore the geometry of the optimized structures by using the dispersion component.

Then, excited energy calculations were rerun with the freshly optimized geometries, and results were compared with previously obtained theoretical results.

When the HOMO-LUMO band gap energies of 7a and 9a were examined, narrower band gap energies were detected compared to the calculations done without using this dispersion component. The band gap energy values obtained both without and using the dispersion component tend to decrease or increase in the same way as the experimental study. However, it is seen that the band gap value obtained by adding the dispersion component deviates further from the experimental data.

Table S-I. The results of the calculations with and without the dispersion component

		Calculation with dispersion component		Calculation without dispersion component	
Compound	Phase	The sum of thermal and free energy (Hartree)	Band gap energy (eV)	The sum of thermal and free energy (Hartree)	Band gap energy (eV)
7a	Gas	-1469.9010	2.85	-1469.7861	2.85
	DMSO	-1469.9125	2.66	-1469.7974	2.87
9a	Gas	-1355.5595	3.22	-1355.4612	3.20
	DMSO	-1355.5644	3.04	-1355.4801	3.19