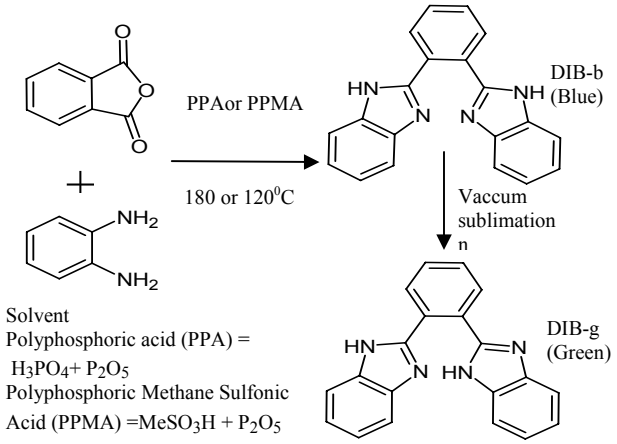
Supplementary Material (ESI) for Chemical Communications

SUPPORTING INFORMATION

Blue to green shifted fluorescence in inter and intra molecular hydrogen bonded Di(benzimidazol-2-yl)benzene

Bijayalaxmi Jena, S. Sundar Manoharan*



Scheme1: Shows the synthesis of Di(benzimidazol-2-yl) benzene. DIB-b isomer on vacuum sublimation converts to DIB-g isomer

Synthesis Procedure:
Stoichiometric amounts of analaR grade reagents, phthalic anhydride and o-phenylenediamine were taken along with a calculated amount of polyphosphoric acid or poly phosphoric methane sulfonic acid in a round bottom flask with a mechanical stirrer. Use of polyphosphoric acid is recommended because of its dual role as solvent and as acid catalyst. Reactions were carried out in N_2 atmosphere and the reaction temperature was ~150-190^{o}C for PPA and 120^{o}C for PPMA. After the reaction, the reaction mixture was poured into cold water and filtered. The product was recrystallized to get a white product (showing blue emission) which on vacuum sublimation yields a greenish-yellow product. Total reaction time was approximately 24-30 hrs

^{1}H-NMR (400MHz) (DIB-b) ($CDCl_3$): 7.46-7.40 (m,2H); 7.10-7.04(m,2H); 6.94-6.88 (m,4H); 6.63-6.57(m,4H); MS $C_{20}H_{14}N_4$ $[M+H]^+$ m/z(%) = 311.1299 (100), Calcd. Mass 311.1297.
(DIB-g) ($CDCl_3$): 7.88-7.80 (m,4H); 7.72-7.64(m,2H); 7.56-7.54 (m,2H); 7.37-7.24(m,4H); MS:$C_{20}H_{14}N_4$ $[M+H]^+$ m/z(%) = 311.1297 (100), Calcd. Mass 311.1297

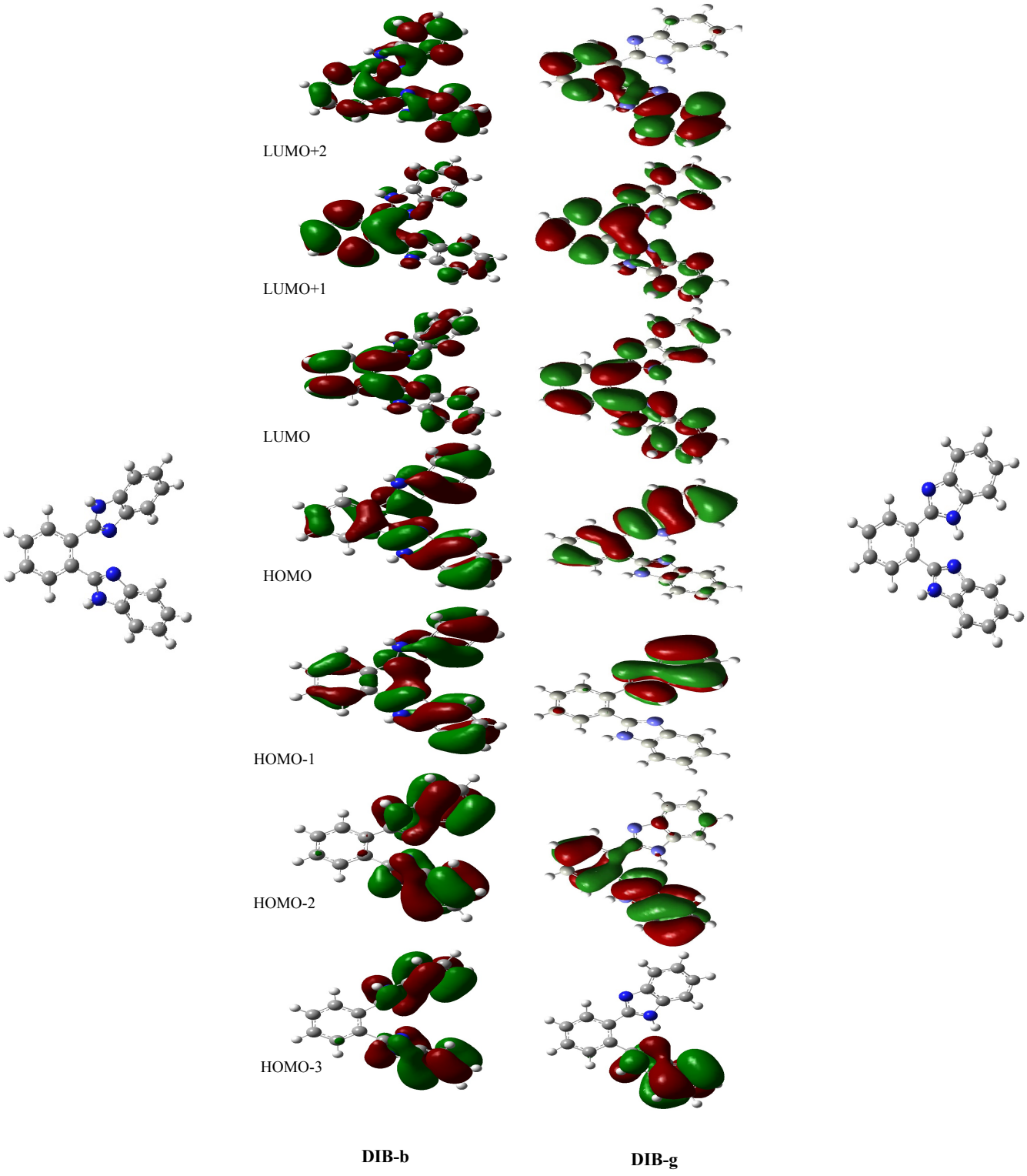


Figure 1: Frontier Molecular Orbitals of DIB-b and DIB-g from HOMO-3 to LUMO+2 level showing more unsymmetrical charge distribution in the ground state goemetry for Str.2 i.e, DIB-g and almost symmetrical charge distribution for Str.1 i.e. DIB-b

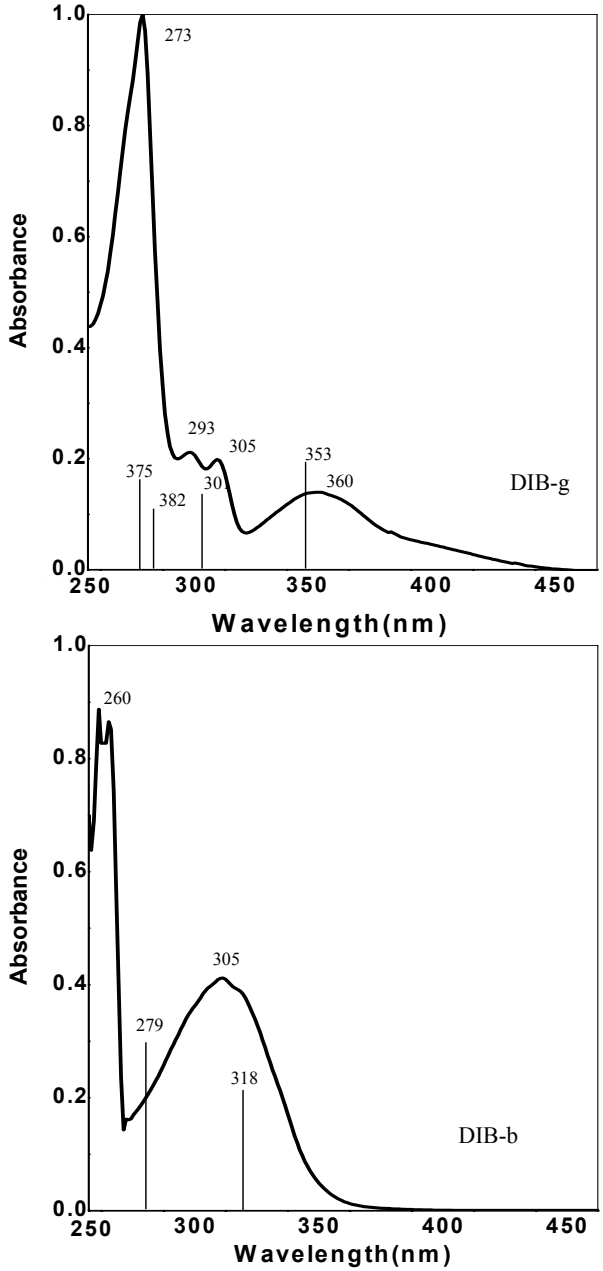


Figure 2: Shows UV-Visible Absorption Spectra of DIB-g (above) and DIB-b (below) in $CHCl_3$ obtained experimentally and the UV-Visible Line Spectrum calculated for DIB-g and DIB-b by TD-DFT Calculation is shown as vertical lines.Note the excellent agreement in the absorption data between the experimental and theoretical peak maximas.

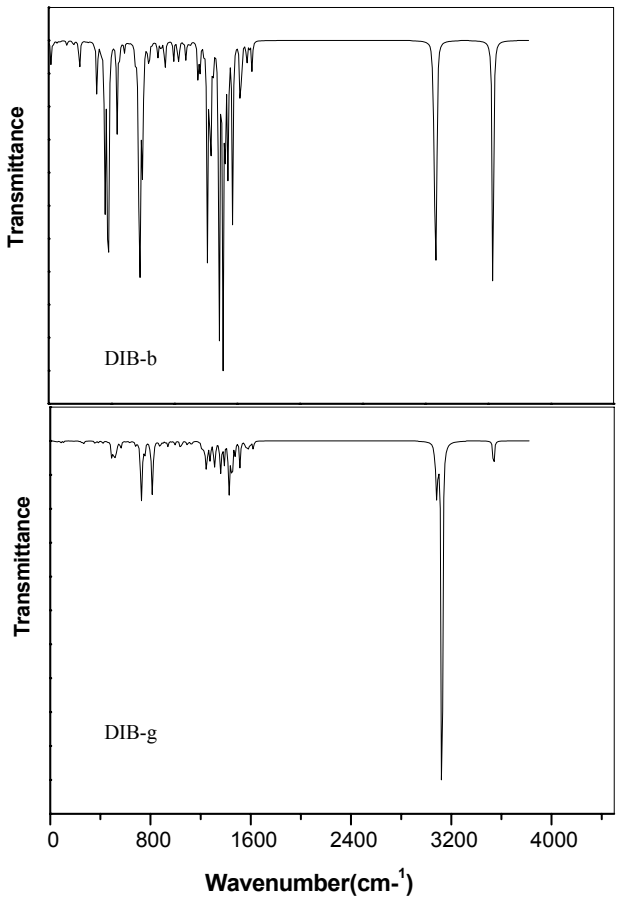


Figure3. Theoretical IR spectra for DIB-b and DIB-g obtained by DFT calculation using B3PW91 functional and 6-31G** as basis set.

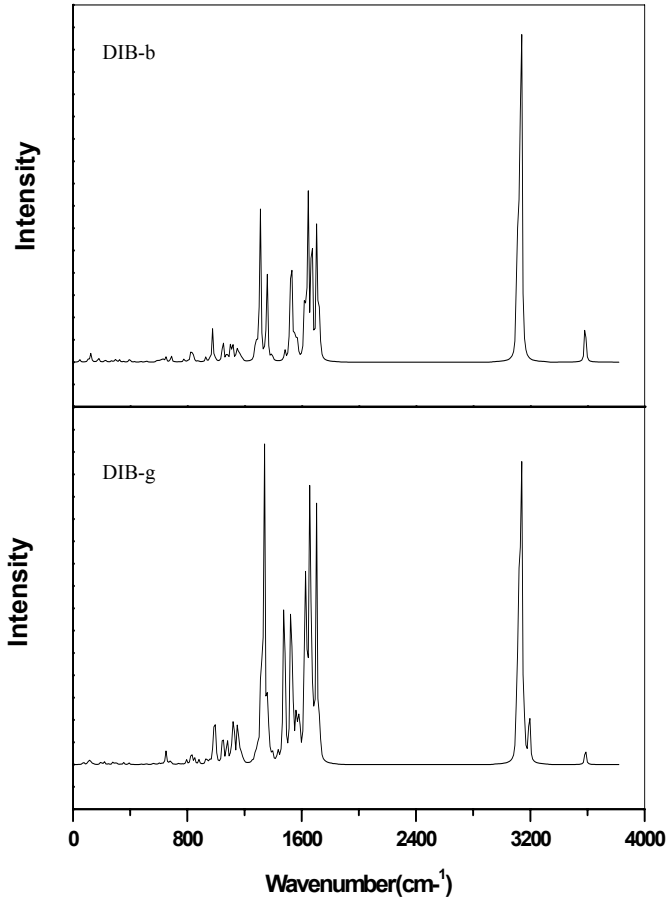


Figure4. Theoretical Raman spectra for DIB-b and DIB-g obtained by DFT calculation using B3PW91 functional and 6-31G** as basis set.

Table1: . Experimental and Calculated Vibrational frequencies and their tentative assignments

Assign ment	DIB-g		DIB-b	
	FTIR obs / cal	Raman cal	FTIR obs / cal	Raman Cal
N-H Strc.	3442 / 3543	3543	3449 / 3552	3581
C-H Strc.	3164 / 3118	3118	----- / 3180	3135
”	3055 / 3074	3074	3056[a] / -----	-----
”	2899 / ----	----	2669[a] , 2426[a]	-----
----	1759, 1728 / --	----	------	1701
C=N, C=C Strc.	1609 / 1621	1621	1650 / 1615	1667, 1643
N-H ipb	1563 / 1593	1593	1521 / 1521	1524
C-C Strc.	1453 / 1443	1443	1439 / 1481	-----
C-N Strc.	1412 / 1410	1410	1429 / 1440	-----
”	1360 / 1373	1373	1360 / 1360	1356
”	1248 / 1264	1264	1233 / 1265	1322
C-H ipb	1138 / 1140	1140	1124 / 1171	1153,1110
”	1070 / 1044	1044	1014 / 1037	1060
C-H opb	946 / 934	934	973 / 997	967, 934
Imidazole ipb	864 / 880	880	878 / 875	824
N-H opb	754 / 742	742	754 / 741	------
Ring ipb	615 / 618	618	618 / 606	698,640
”	522 / 536	536	576 / 539	------
”	481 / 495	495	480 / 485	------

a = strong broadening, strc= stretching, ipb=in plane bending, opb=out plane bending