

## Supporting Information

for

### **A proton-assisted AIE active luminescent material having tunable emission in solution and solid state with anti-counterfeiting application: Smart high contrast on-off-on fluorescence switch**

Asit Mondal\* and Pabitra Chattopadhyay\*

Department of Chemistry, The University of Burdwan, Golapbag, Burdwan 713104, India.

*E-mail: [pabitracc@yahoo.com](mailto:pabitracc@yahoo.com)*

## CONTENTS

- 1. Fig. S1**  $^1\text{H}$  NMR (400 MHz) spectra of **DPABHz** in  $\text{CDCl}_3$
- 2. Fig. S2**  $^{13}\text{C}$  NMR (100 MHz) spectra of **DPABHz** in  $\text{DMSO-D}_6$
- 3. Fig. S3** High resolution mass spectrum of **DPABHz**
- 4. Fig. S4** IR spectra of **DPABHz** showing sharp peak at  $1612\text{ cm}^{-1}$  for  $-\text{C}=\text{N}$  bond
- 5. Fig. S5** Absorption spectra of (A) **DPAB** and (B) **DPABHz** in different solvent
- 6. Fig. S6** (A) Normalized emission spectra of (A) **DPAB** and (B) **DPABHz** in different solvents,  $\lambda_{\text{ex}}=363\text{ nm}$ .
- 7. Fig. S7** Absorption spectra of (A) **DPAB** and (B) **DPABHz** in THF/water mixture with varying percentage of water in THF
- 8. Fig. S8** Absorption spectra of (A) **DPAB** and (B) **DPABHz** upon incremental addition of acid
- 9. Fig. S9** SEM images of **DPABHz** (A) before and (B) after protonation
- 10. Table S1** The binding energy calculated using Hatree Fock (HF) method at 6-31G(d) level of theory in Gaussian 09 program

**11. Table S2** Optimized structure, corresponding dipole moment ( $\mu$ ) and Electrostatic potential (ESP) of **DPAB** and **DPABHz** in different solvent

**12. Fig. S10** Theoretical UV-Vis spectra (A) **DPAB**; (B) **DPABHz** (towards  $-\text{NH}_2$  group) and (C) **DPABHz** (at triphenyl N) obtained from TDDFT calculation at the B3LYP/6-31+G(d,p) level of theory in THF.

## Experimental Section

### Materials and methods

All reagents and chemicals herein were received from Aldrich and Merck companies and used without further purification. All the solvents used were spectroscopic grade. The  $^1\text{H}$  NMR spectra and  $^{13}\text{C}$  NMR spectra were measured on a Bruker Avance 400 MHz and 100 MHz spectrometer, respectively, and TMS was used as an internal standard. Qtof Micro YA263 mass spectrometer was used to record the electron spray ionization (ESI) mass spectra. IR instruments were used for the measurement of Fourier-transform infrared (FTIR) spectroscopy. Systronics digital pH meter (model 335) was used for pH measurement. Optical fluorescence microscopy (OFM) images were taken in LEICA DM1000 LED upright microscope equipped with CCD camera (model no. DS-Fil). Perkin Elmer LS55 fluorescence spectrophotometer was used to obtain the fluorescence spectra in the solid state.

### General Method of Spectral Studies

A stock solution of **DPAB** and **DPABHz** in THF solution was prepared to make for spectral analyses. The stock solution (2 mM) of **DPAB** and **DPABHz** was used for absorption and fluorescence experiments after appropriate dilution. Absorption and fluorescence spectra were measured using a Shimadzu -2450 UV-Vis spectrophotometer a HITACHI F-7000 fluorescence

spectrophotometer, respectively, in a 10 mm path length cuvette. During the experiment, the excitation wavelength at 363 nm was selected for to acquire the fluorescence spectra, where the excitation/emission slit was 5 nm. The temperature throughout the experiment was 25 °C and all the spectroscopic measurements were done at room temperature (25 °C). To observe the AIE nature of **DPAB** and **DPABHz**, we have performed UV-Vis and fluorescence experiments using THF/water binary mixture with varying water percentage of water content in THF which is used as good solvent. To observe the AIE nature water was used as a poor solvent. To observe the effect of protonation of **DPAB** and **DPABHz** in solution and solid state, trifluoroacetic acid (TFA) and ammonia (NH<sub>3</sub>) solution were used. To study the optical properties of **DPABHz** in the solid state, mortar and pestle have been used for visual fluorescence colour change under UV-lamp (365 nm). To examine the anti-counterfeiting application, a piece of TLC plate was used.

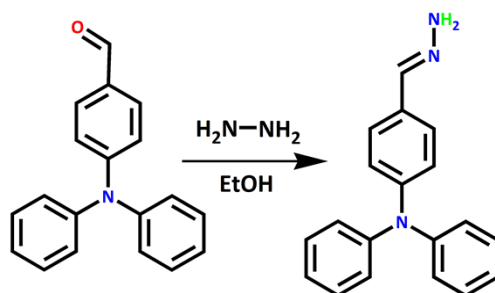
### **Computational Details**

To understand the electronic structure of **DPAB** and **DPABHz**, a density functional theory (DFT) study was carried out. We performed individual geometry optimization of the luminophores (**DPAB** and **DPABHz**) using the density functional theory method at the B3LYP<sup>1-3</sup> level with the Gaussian 09 program package.<sup>4</sup> The split-valence 6-31G+(d,p) was used as a basis set for all the calculations except for the calculation of binding energy. Binding energy calculation was carried out using Hartree-Fock (H) method. For the account of solute-solvent interaction, implicit solvation effect in THF was considered through the conductor-like polarizable continuum model (CPCM).<sup>5</sup> Time-dependent density functional theory (TDDFT) calculations were also performed to predict the UV-Vis spectra, vertical excitation energies, dipole moment spatial distribution of frontier molecular orbitals (FMOs) of the compounds as well as their protonated congener (**DPABHzH<sup>+</sup>**). The same level of calculation was performed using B3LYP/6-31G+(d,p) level of theory for geometry optimization.

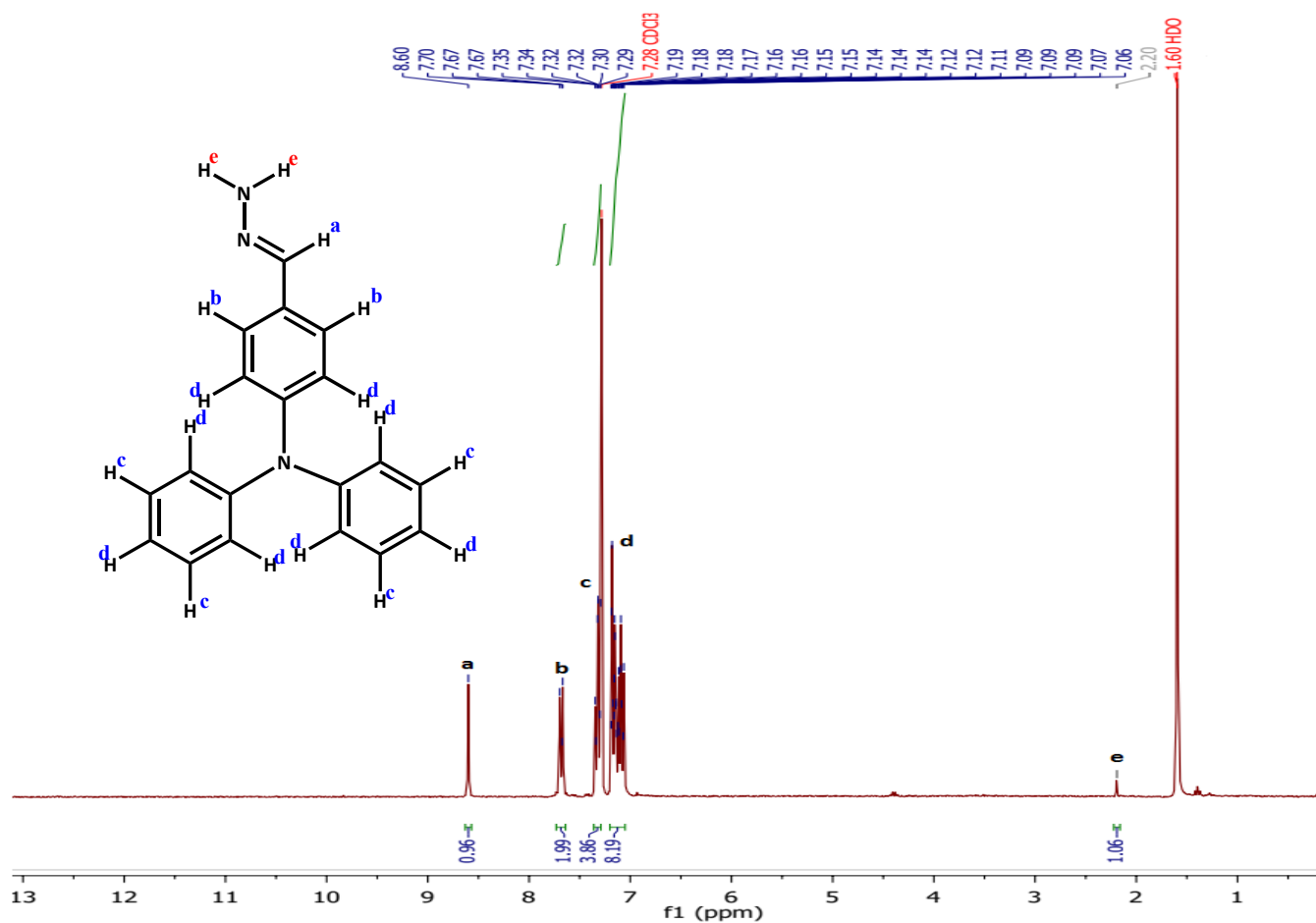
### **Synthesis of (4-hydrazonomethyl-phenyl)-diphenyl-amine (DPABHz)**

To a solution of compounds *4-diphenylamino-benzaldehyde* (546.22 mg, 2 mmol) in EtOH (50 mL), hydrazine hydrate (32.04 mg, 1mmol) was added with continuous stirring for 1 h and the resulting mixture was reflux with 4h at 37°C and yellow solid product (*(4-hydrazonomethyl-phenyl)-diphenyl-amine*) was formed after slow evaporation of EtOH (Scheme S1).

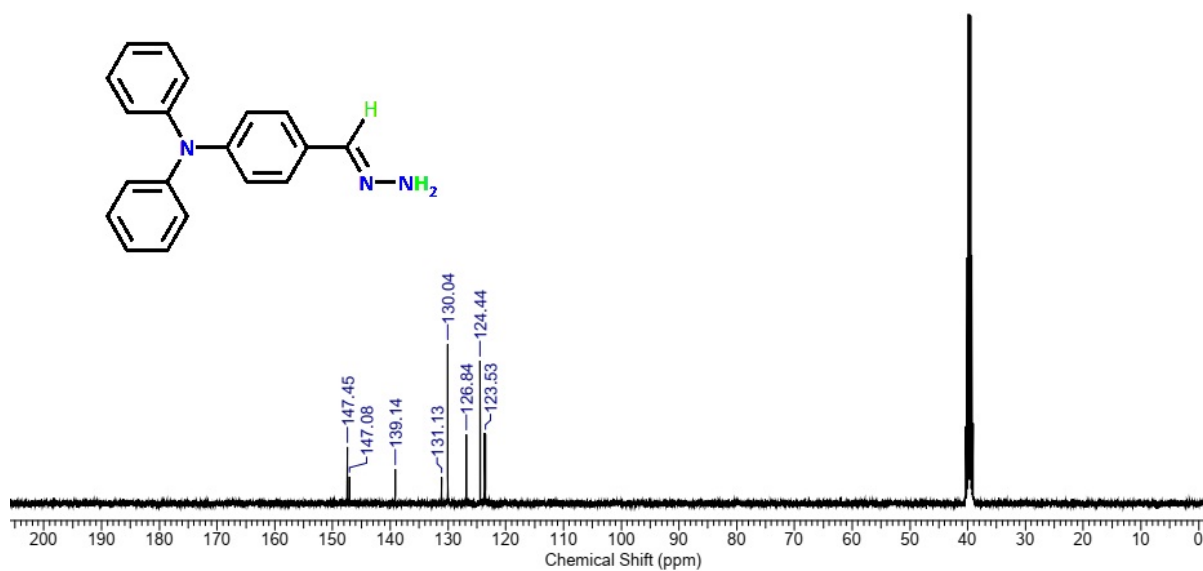
**C<sub>19</sub>H<sub>17</sub>N<sub>3</sub>**: ESI-MS: [M + H]<sup>+</sup>, m/z, 288.1509 (100 %) (calcd.: m/z, 288.1495). <sup>1</sup>H NMR (400 MHz DMSO-d<sub>6</sub>): δ, 8.60 (s, 1H); 7.70-7.67 (d, 2H, J = 12 Hz); 7.35-7.29 (m, 4H, J ≈ 4 Hz); 7.19-7.06 (m, 8H, J ≈ 4 Hz); 2.20 (NH<sub>2</sub>); <sup>13</sup>C NMR (100Hz DMSO-d<sub>6</sub>): δ, 147.45, 147.081, 139.14, 131.13, 130.043, 126.84, 124.44, 123.53, FTIR (KBr, cm<sup>-1</sup>): 1612 cm<sup>-1</sup> for C=N, Yield: ≈ (476.0 mg) 83 % .



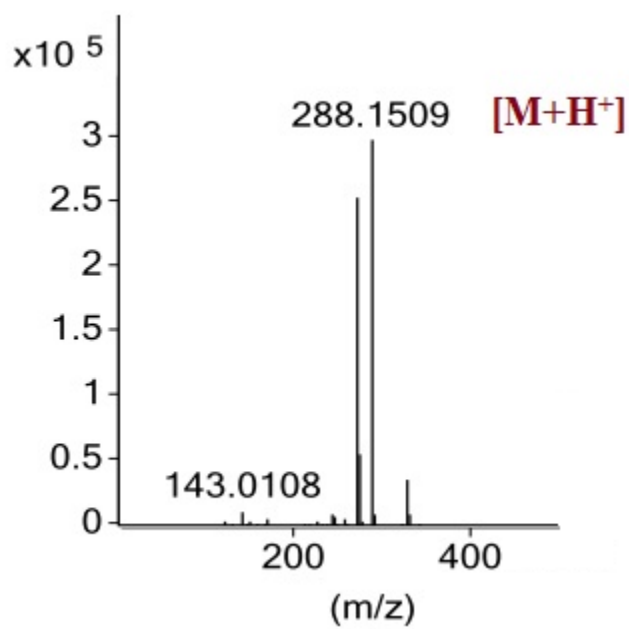
**Scheme S1. Synthetic Route for DPABHz**



**Fig. S1**  $^1\text{H-NMR}$  (400 MHz) spectra of **DPABHz** in  $\text{CDCl}_3$



**Fig. S2**  $^{13}\text{C NMR}$  (400 MHz) spectra of **DPABHz** in  $\text{DMSO-D}_6$



**Fig. S3** High resolution mass spectrum of **DPABHz**:  $[\text{M}+\text{H}]^+$ : (calcd. 288.1495) where **DPABHz** = **M**

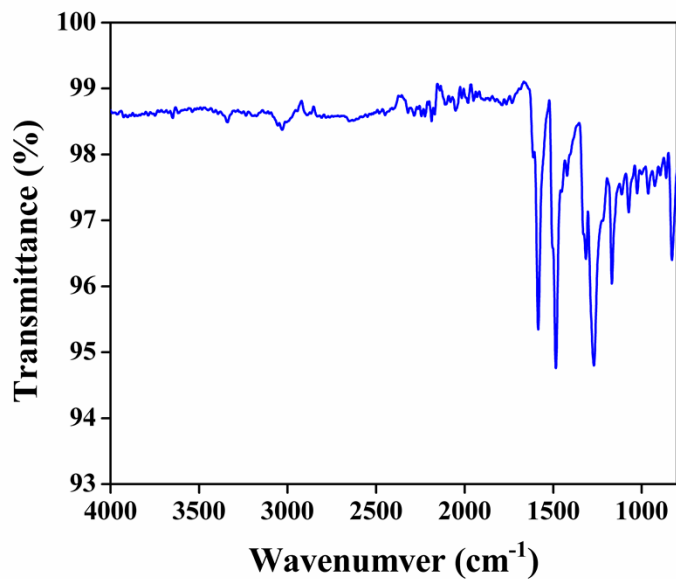


Fig. S4 IR spectra of DPABHz

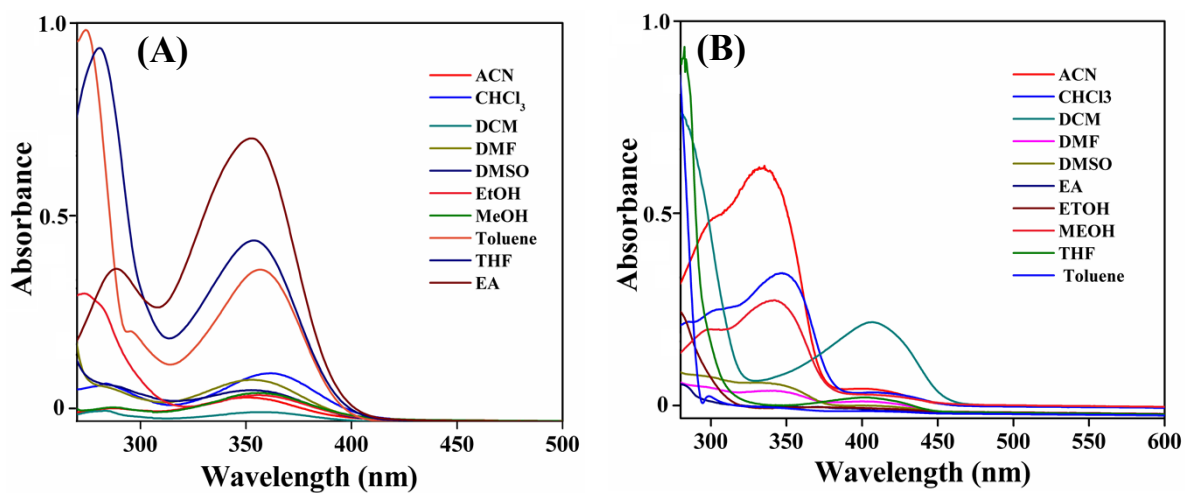


Fig. S5 Absorption spectra of (A) DPAB and (B) DPABHz in different solvent

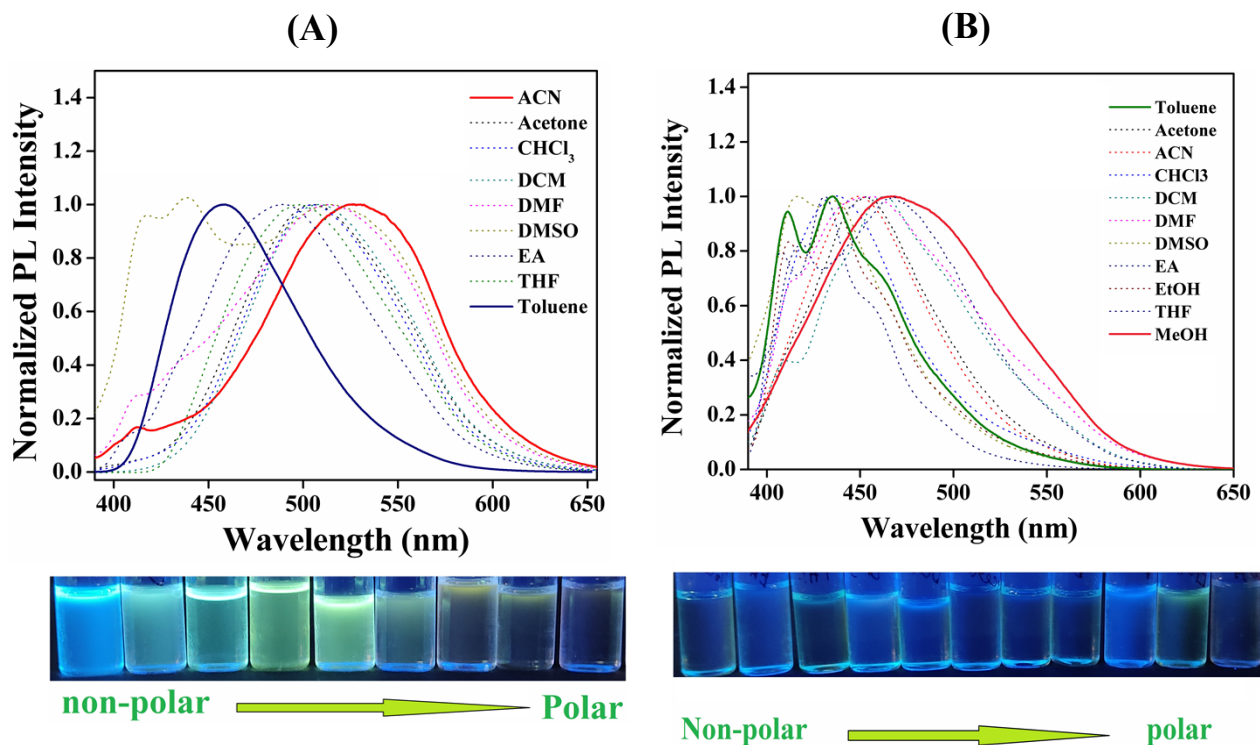


Fig. S6 (A) Normalized emission spectra of (A) DPAB and (B) DPABHz in different solvents,  $\lambda_{\text{ex}}=363$  nm.

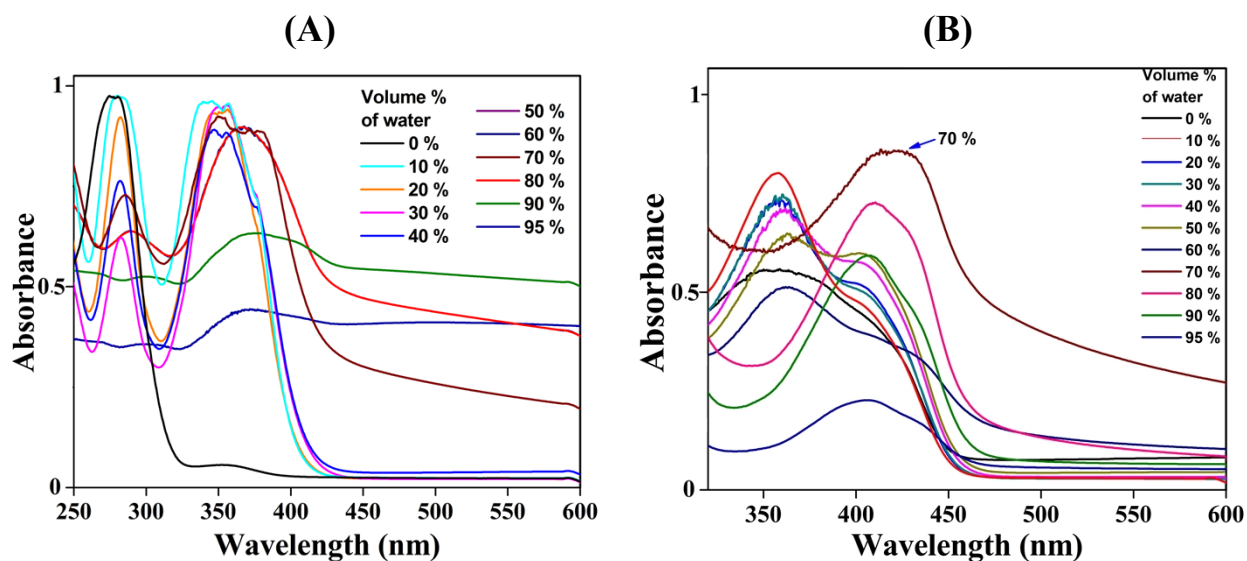
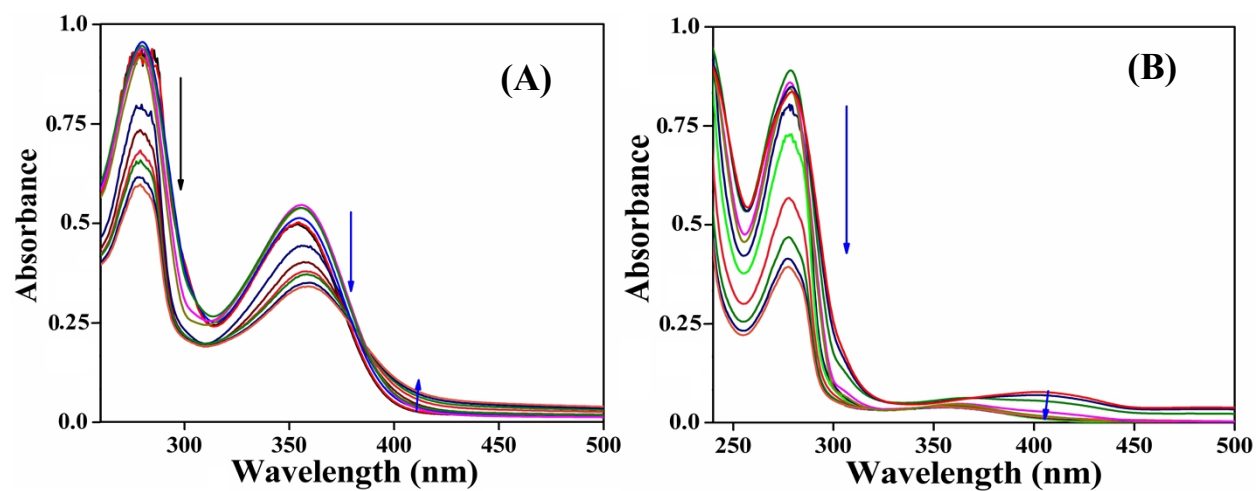
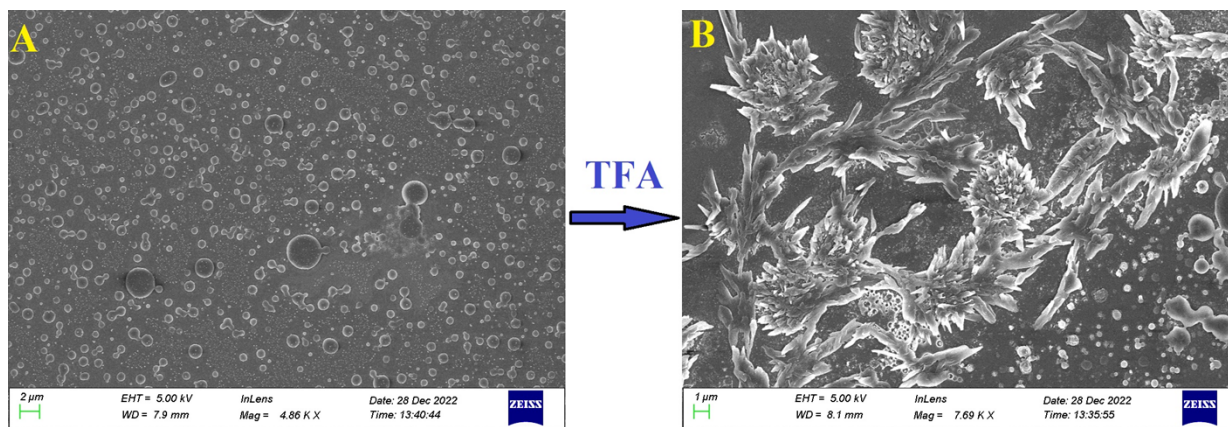


Fig. S7 Absorption spectra of (A) DPAB and (B) DPABHz in THF/water mixture with varying percentage of water in THF



**Fig. S8** Absorption spectra of (A) DPAB and (B) DPABHz upon incremental addition of acid



**Fig. S9** SEM images of DPABHz (A) before and (B) after protonation



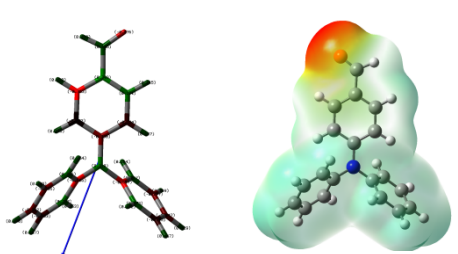
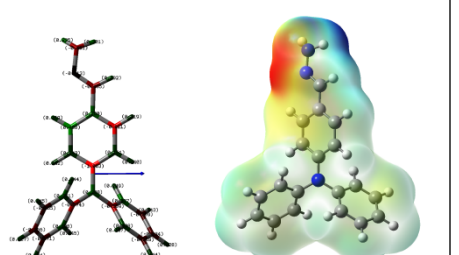
**Table S1** The binding energy calculated using Hatree Fock (HF) method at 6-31G(d) level of theory in Gaussian 09 program

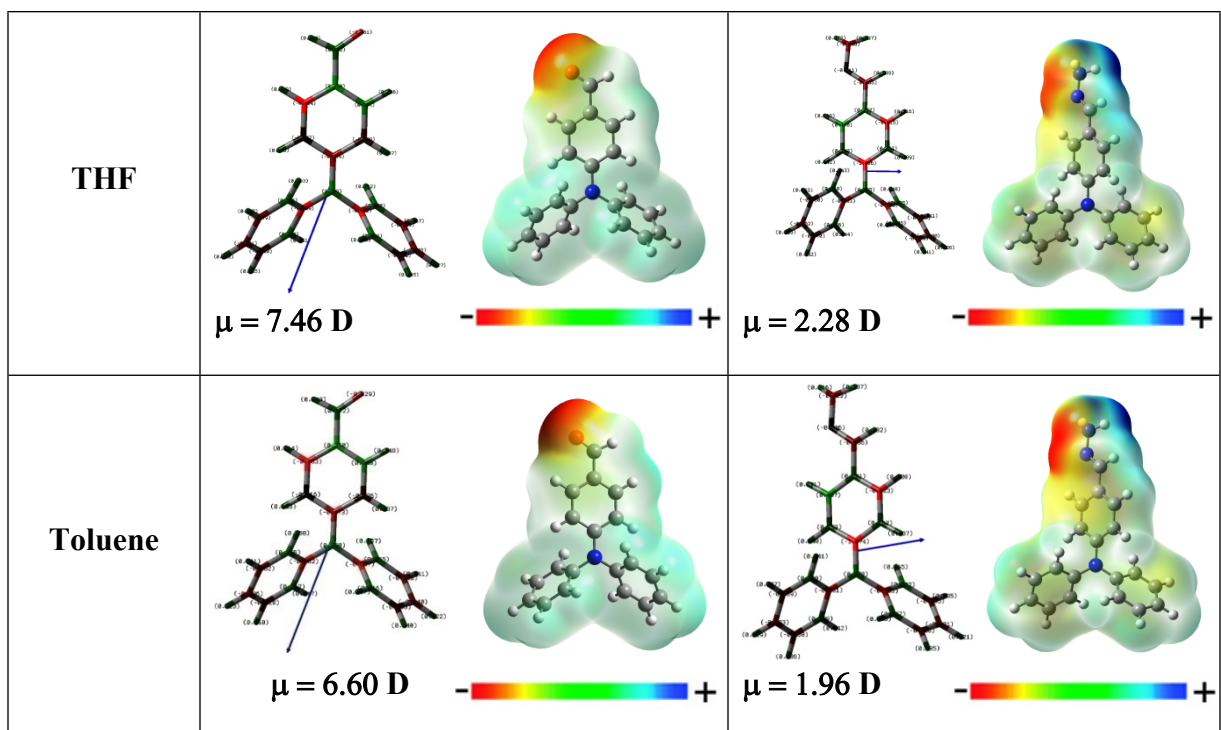
Compounds	Opt. Energy Kcal/mol	E <sub>bind</sub> (Kcal/mol)
DPAB	-558704.5674	
DPAB H <sup>+</sup>	-558972.8759	-174.3326876
DPABHz	-581607.3814	
DPABHzH <sup>+</sup> (triphenyl N)	-581879.7946	-178.4373635
<b>DPABHzH<sup>+</sup> (towards -NH<sub>2</sub> group)</b>	-581891.5377	<b>-190.1804468</b>
H <sup>+</sup>	-93.97584814	

The equation (1) is used to calculate the binding energy of the corresponding species mention in Table S1

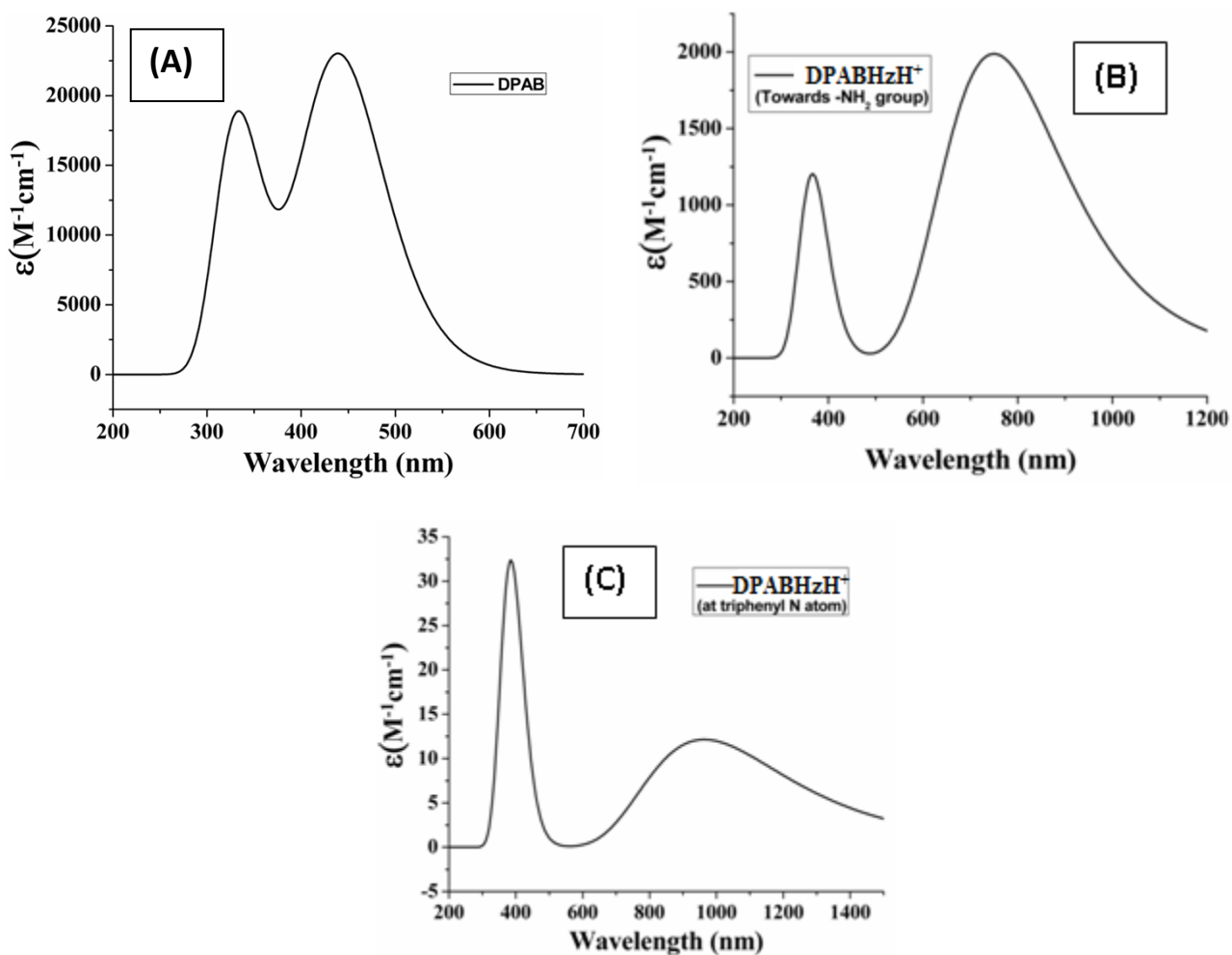
$$E_{\text{bind}} = E_{\text{opt-dimer}} - (E_{\text{opt-mon1}} + E_{\text{opt-mon2}}) \quad \dots(1)$$

**Table S2** Optimized structure, corresponding dipole moment ( $\mu$ ) and Electrostatic potential (ESP) of DPAB and DPABHz in different solvent

Solvent	DPAB ( $\mu$ )	DPABHz ( $\mu$ )
DMSO	 $\mu = 7.89 \text{ D}$	 $\mu = 2.36 \text{ D}$



D stands for Dipole moment



**Fig. S10** Theoretical UV-Vis spectra (A) DPAB; (B) DPABH $z\text{H}^+$  (towards -NH $_2$  group) and (C) DPABH $z\text{H}^+$  (at triphenyl N) obtained from TDDFT calculation at the B3LYP/6-31+G(d,p) level of theory in THF.

## References

- 1 A. D. Becke, Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.*, 1993, **98**, 5648-5652.
- 2 C. Lee, W. Yang and R. G. Parr, Development of the Colle-Salvetti Correlation-energy Formula into a Functional of the Electron Density. *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1988, **37**, 785-789.
- 3 P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J. Phys. Chem. A*, 1994, **98**, 11623-11627.
- 4 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson et al. Gaussian 09, revision A.01; Gaussian, Inc.:Wallingford CT, 2009.
- 5 M. Cossi, N. Rega, G. Scalmani and V. Barone, *J. Comput. Chem.* 2003, **24**, 669–681.