Surface Engineering of CsPbBr$_3$ Perovskite Nanocrystals: Hole Transfer Dynamics and Enhanced Photocurrent Response Using Novel Organic Molecule

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Experimental Section:

Materials and instrumentation

9H-fluorene, 2-Bromo Ethane, and KOH were purchased from Sigma-Aldrich. We used anhydrous solvents for the reaction. All other chemicals used in this work were analytical grade and were used without further purification. All organic reactions were performed under an inert atmosphere. Cesium carbonate (Cs_2CO_3, 99.9%), lead acetate (Pb $(OAc)_2$, 98%), lead bromide ($PbBr_2$, 98%) oleic acid (OA, 90%), oleylamine (OAm, 90%) were purchased from Alfa Aesar. 1-octadecene (ODE, 90%), Bromopropane (Br-Propane, 99%), and n-trioctylphosphine (TOP, 90%) were purchased from Sigma Aldrich. No further purification was done for the chemicals used in the experiments. No gassing/degassing steps of the inert gas were done for PNCs synthesis. They were performed in completely open-air conditions.
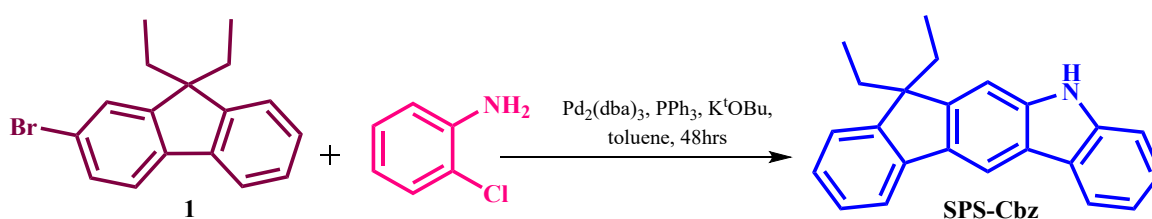
Synthesis of 1:

2-Bromo Ethane (3.15g, 20 mmol) was added to the solution of compound 1 (200mg, 8.15 mmol) and KOH (2.28 g, 40.79 mmol) in DMSO media. The reaction was carried out for 24 hrs at RT. After completion of the reaction, the solvent was evaporated using a vacuum, and extra DMSO was removed during the workup process using ice water and DCM. The crude product was purified using column chromatography on silica. (Yield:80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ= 7.72-7.68 (m, 1H), 7.62-7.56 (m, 1H), 7.52-7.48 (m, 2H), 7.40-7.32 (m, 3H), 2.02-1.58 (m, 4H), 0.4 (t, 6H), ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 151.593, 149.82, 141.49, 129.722, 136.796, 127.465, 126.732, 126.957, 122.851, 119.579, 115.507, 114.939, 56.078, 32.781, 29.704, 22.697, 14.121, 8.318. ESI-MASS calculated for $C_{17}H1_7Br$ (M^+): 300.05.
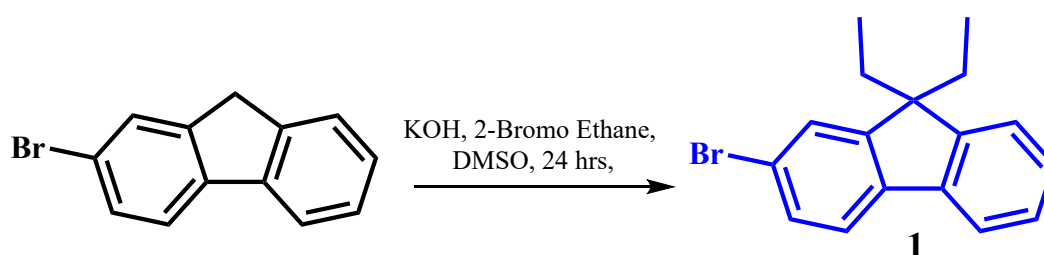
Synthesis SPS-Cbz:

The sealed tube with **1** (500 mg, 1.66 mmol), 2- Chloroanline (573 mg, 3.32 mmol), K^{t}BuO (800mg, 8.30 mmol), Pd$_2$ (dba)$_3$, and toluene was refluxed for 48 hrs at 100^{0}c. After 48hrs, the solvent was concentrated using a rotary evaporator, did the workup process using an organic solvent. The crude product was subjected to purification using stationary phase silica and

mobile phase. (Yield:80%) ^{1}H NMR (500 MHz, CDCl$_3$) δ= 7.66-7.62 (m, 2H), 7.58-7.50 (m, 1H), 7.34-7.10 (m, 5H), 7.16-7.10 (m, 2H), 2.40-1.92 (m, 4H), 0.4 (m, 6H), ^{13}C NMR (100.62 MHz, CDCl$_3$) δ 151.339, 149.26, 141.692, 141.006,140.223, 133.532, 132.704, 128.422, 126.57, 126.061, 122.526, 119.569, 118.771,115.384,114.875, 111.441, 55.817, 32.509, 8.276. ESI-MASS calculated for C$_{13}$H$_{21}$N (M$^+$): 311.16.

Synthesis of Cesium-oleate solution:

For synthesizing the Cesium-oleate solution, Cs$_2$CO$_3$ of 0.2 g with 0.61 mmol, OA of 0.88 mL with 0.5 mmol, and ODE of 7.5 mL were taken in the glass vial and kept at 120 ºC temperature with continuous stirring for 1 hour, after dissolving the Cs$_2$CO$_3$ salt, until it gets the clear solution. It was again preheated before use as it reached the principate at room temperature. The final concentration of Cesium oleate is 0.0732 M.

Synthesis of completely amine-free CsPbBr$_3$ PNCs:

For the synthesis of amine-free CsPbBr$_3$, PNCs were adopted for our previous work.[1] In a glass vial, 2 mL of ODE, 0.25 mL of OA with 0.79 mmol, and Pb(OAc)$_2$ of 0.062 g with 0.188 mmol were taken and kept at 100 ºC until the Pb(OAc)$_2$ got dissolved and forms the lead oleate solution. Then 0.5 mL TOP was added with the Br-Propane of 68.3 µL with 0.752 mmol; after

getting the clear solution temperature was raised to 150-160 ºC, and then 0.4 mL of Cs-oleate was swiftly injected into the reaction mixture. After 30 sec of the reaction, it was quenched into the ice water bath, and bright green CsPbBr$_3$ PNCs were formed. Finally, the as-synthesized CsPbBr$_3$ PNCs were centrifuged, the precipitate was dispersed in the toluene, and the supernatant was discarded.

Synthesis of amine-CsPbBr$_3$ PNCs:

For the synthesis of amine-CsPbbr$_3$ PNCs was adopted from our previously reported work.[2] In short, a glass vial of PbBr$_2$ of 0.069 g with 0.188 mmol, 0.5 mL of OA, and OAm with 5 mL of ODE was taken and kept at 120 ºC and heated until the PbBr$_2$ was completely dissolved and then the temperature was raised to 140 ºC. Then 0.4 mL of Cs-Oleate was injected rapidly into

the reaction mixture, and after 2 min, the yellowish-green color solution was formed by quenching the reaction by putting it in an ice-water bath. Finally, the crude CsPbBr$_3$ PNCs were centrifuged, the supernatant was discarded, and the precipitate was dispersed in toluene.

Steady-State Experiment:

First, SPS-Cbz molecules were dissolved in solvent using toluene to prepare the 10 mM solution of hole donor. In the PL cuvette, a significant amount of amine-free CsPbBr$_3$ PNCs suspension was added and followed by the different amounts of the SPS-Cbz solution (0, 2.5, 5, 10, 25, 50, 75, 100, 125, and 150μL for 0, 0.01, 0.02, 0.04, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 mM) was added into the PNCs. Finally, the total volume was made to 3 mL by adding sufficient toluene to the cuvette. The exact process was followed for amine CsPbBr$_3$ PNCs.

Characterization & Instrumentation:

All the as-synthesized two different surfaces capped CsPbBr$_3$ PNCs were dispersed in toluene. UV-Vis data and fluorescence spectra were recorded in a 1 cm path length quartz cell on a Shimadzu UV-vis near IR 3600 spectrometer and FlouroLog-3 Horiba Jobin Yvon was used to measure the photoluminescence (PL) spectra. Using the cumarine 153 dye molecule in ethanol with QY=0.156 as a reference, photoluminescence quantum yield PLQYs were calculated. The well-cleaned glass substrate was drop cast with the as-synthesized PNCs to measure the powder X-ray diffraction (PXRD) patterns using the Empyrean PANalytical X-ray Diffractometer usiKα X-radiation (λ = 1.5406 Å) at 40 kV and 30 mA power. A drop of an optimum solution of NCs in hexane was coated on the copper (Cu) grid coated with the carbon film, which was used for transmission electron microscopy images with JEOL JEM-2100 High-Resolution Transmission Electron Microscope with 0.23 nm point resolution. Bruker Alpha II spectrometer with broadband MCT detector was used to measure with the ATR-FTIR Attenuated total reflection - Fourier transforms infrared spectroscopy mode. Time-correlated single-photon counting by TCSPC spectrometer with Horiba Jobin Yvon IBH was used to measure the time-resolved photoluminescence measurements using the laser diode with an output of 372 nm of the excitation source. The prompt of the lamp was recorded using the dilute solution of Ludox in water as scattering in the sample chamber. IBH DAS6 software was used for the fluorescence decay fitting curves analyzed.

Bi-exponential fits of the TCSPC data with the equation:

$$f(t) = A_1 e^{-\frac{t}{\tau_1}} - A_2 e^{-\frac{t}{\tau_2}}.$$

$\bar{\tau}$ is the intensity-averaged lifetime from a Bi-exponential fit using the equation:

$$\bar{\tau} = \sum \alpha_i * \tau_i^2 / \sum \alpha_i * \tau_i.$$

$$K_r = PLQY/\bar{\tau}_{avg}$$

$$K_{nr} = (1-PLQY)/\bar{\tau}_{avg}$$

Electrochemical studies are done using Cyclic Voltammetry by a three-electrode conventional method and a BAS100 electrochemical analyzer. Pt rod was the working electrode, a Pt wire was the auxiliary (counter) electrode, Ag/AgCl was the reference electrode, and 0.1 M tetrabutylammonium hexafluorophosphate was a supporting electrolyte.

Photoelectrochemical Measurements:

Photocurrent measurements were performed using a three-electrode system CH Instruments Inc., USA, CHI6005E electrochemical workstation with a temperature-controlled potentiostat. Platinum wire as a counter electrode, saturated Ag/AgCl electrode as reference electrode (in 3M, KCl solution), and working electrode as our PNCs as a catalyst by making a film on the ITO substrate with the artificial solar simulator of AM 1G illuminator (100mW cm^{-2}) light source was used for measurement. These three electrodes were kept in the quartz cell with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) in Ethyl acetate. The photocurrents were measured using the CHI workstation instrument under the light irradiation of white light at a potential of 0.02 V.

Computational Details

Time-Dependent DFT (TDDFT) and Density Functional Theory (DFT) calculations were performed using the *Gaussian09* program.[3] The SPS-Cbz with a neutral charge was optimized in the gas phase. B3LYP exchange-correlation functional with Hay and Wadt's double zeta quality Los Alamos electron effective core potential basis set 6-311 g (d,p) was adopted on all atoms.[4–6] The optimized geometries were analyzed by vibrational frequencies, resulting in no imaginary frequencies. Thus, the optimized structures correspond to absolute minima on the potential energy surface. At the optimized geometry, TDDFT calculations were performed at the B3LYP/6-311 g (d,p) level of theory in dichloromethane solvent utilizing the Polarizable Continuum Model[7,8] (PCM), as implemented in *Gaussian 09*.50 singlet-singlet excitations at S$_0$ optimized geometry are calculated. *GaussSum 2.2.5*[9] was used to simulate a significant portion of the absorption spectrum and interpret the transition nature. The *Gaussview*[10] was

used to make molecular orbital surfaces, and *GaussSum* software was used to calculate the percentage contributions of the SPS-Cbz molecular orbitals.

Table S1. Experimental λ $_{max}$, calculated λ $_{max}$, (nm) and oscillator strengths (f) of SPS-Cbz calculated at B3LYP/6-311g (d,p) in DCM solvent

State	Wavelength (nm)	Osc. Strength	Major Contributions	Minor Contributions
S1	328.215	0.0965	HOMO->LUMO (83%)	H-1->LUMO (7%), H-1->L+1 (4%),
S2	318.469	0.0406	H-1->LUMO (63%), HOMO->LUMO (11%), HOMO->L+1 (23%)	
S3	294.099	1.738	H-1->LUMO (28%), HOMO->L+1 (69%)	
S4	280.353	0.1522	H-1->L+1 (75%), HOMO->L+2 (14%)	H-2->LUMO (2%)
S5	267.840	0.0245	H-2->LUMO (73%)	H-1->L+1 (8%), H-1->L+2 (8%), HOMO->L+2 (7%)
S6	258.729	0.1744	H-2->LUMO (15%), HOMO->L+2 (57%)	H-3->LUMO (3%), H-2->L+1 (5%), H-1->L+1 (8%), H-1->L+2 (2%), H-1->L+3 (3%)
S7	252.326	0.1706	H-1->L+2 (75%), HOMO->L+2 (11%)	H-2->LUMO (3%), H-2->L+1 (6%), HOMO->L+3 (2%)
S8	251.7428	0	H-1->L+4 (29%), HOMO->L+4 (64%)	H-2->L+4 (6%)
S9	243.706	0.1566	H-3->LUMO (37%), H-2->L+1 (31%)	H-2->LUMO (2%), H-1->L+2 (9%), H-1->L+3 (8%), HOMO->L+2 (7%)
S10	240.426	0	H-1->L+4 (66%), HOMO->L+4 (31%)	
S11	239.308	0.0423	H-3->LUMO (23%), H-2->L+1 (14%), HOMO->L+3 (53%)	H-1->L+3 (3%)
S12	234.0279	0.1381	H-3->LUMO (30%), H-2->L+1 (16%), HOMO->L+3 (30%)	H-1->L+2 (2%), H-1->L+3 (4%), H-1->L+5 (2%), HOMO->L+5 (6%)
S13	228.490	0.1026	H-3->L+1 (11%), H-2->L+1 (17%), H-1->L+3 (63%)	
S14	225.740	0.003	H-3->L+1 (69%)	H-2->L+2 (7%), H-1->L+3 (6%), HOMO->L+3 (3%),
S15	216.0327	0.1237	H-2->L+2 (10%), HOMO->L+5 (47%)	H-4->LUMO (5%), H-4->L+1 (5%), H-3->L+2 (5%), H-2->L+3 (4%)

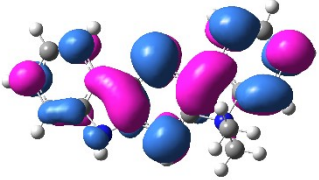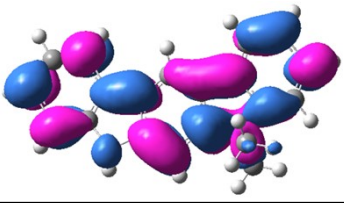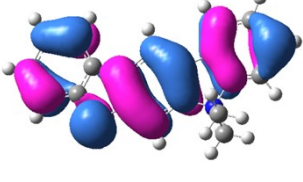**Table S2.** Molecular orbital pictures of SPS-Cbz calculated at B3LYP/6-311g (d,p) level of theory.
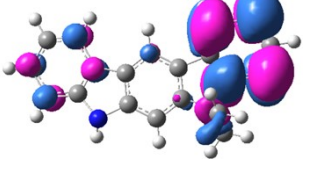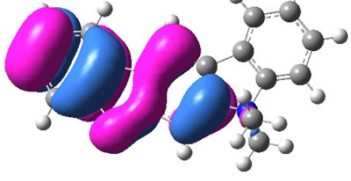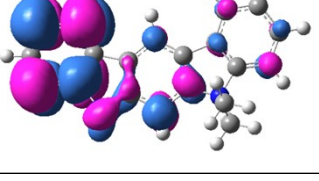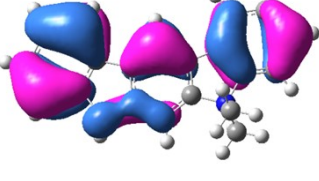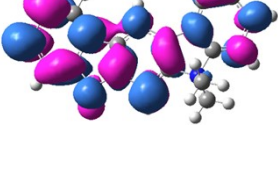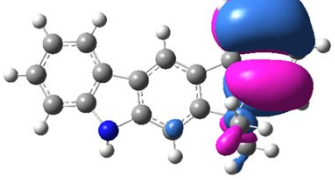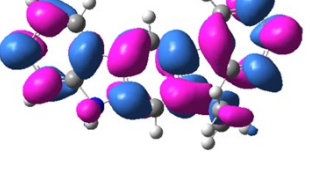
SPS-Cbz				
HOMO	Cbz (78%) IND (22%)	LUMO	Cbz (62%) IND (38%)	
HOMO-1	Cbz (17%) IND (53%)	LUMO+1	Cbz (94%) IND (06%)	
HOMO-2	Cbz (24%) IND (76%)	LUMO+2	Cbz (12%) IND (88%)	
HOMO-3	Cbz (40%) IND (60%)	LUMO+3	Cbz (80%) IND (20%)	
HOMO-4	Cbz (99%) IND (01%)	LUMO+4	Cbz (59%) IND (41%)	

Table S3: PL lifetime-decay curves from TCSPC spectra with their parameter of amine-free capped $CsPbBr_3$ PNCs with the addition of different concentrations of SPS-Cbz molecules.

Sample (mM)	α_1	τ_1 (ns)	α_2	τ_2 (ns)	$\bar{\tau}_{avg}$ (ns)	PLQY (%)	K_r/ ns^{-1}	K_{nr}/ ns^{-1}
0	0.75	7.66	0.25	33.78	23.20	80.14	0.034544	0.00856
0.01	0.75	7.42	0.25	32.76	22.51	62.86	0.027929	0.016495
0.02	0.76	7.4	0.24	30.89	20.75	51.76	0.024947	0.023246
0.04	0.76	6.89	0.24	28.73	19.30	42.18	0.021855	0.029958
0.1	0.76	6.01	0.24	26.52	17.95	35.92	0.020012	0.035698
0.2	0.78	4.62	0.22	19.78	12.91	18.87	0.014624	0.062835
0.3	0.81	3.75	0.19	17.12	10.66	7.42	0.006966	0.086842
0.4	0.81	2.06	0.19	10.07	6.33	5.28	0.008352	0.149626
0.5	0.83	1.71	0.17	9.14	5.59	2.16	0.003868	0.175023
0.6	0.85	1.21	0.15	6.89	4.05	1.13	0.002798	0.244116

Table S4: PL lifetime-decay curves from TCSPC spectra with their parameter of amine capped $CsPbBr_3$ PNCs with the addition of different concentrations of SPS-Cbz molecules.

Sample (mM)	α_1	τ_1 (ns)	α_2	τ_2 (ns)	$\bar{\tau}_{avg}$ (ns)	PLQY (%)	K_r/ ns^{-1}	K_{nr}/ ns^{-1}
0	0.79	3.96	0.21	15.38	9.76	85.24	0.0873	0.0152
0.01	0.79	3.81	0.21	14.59	9.24	84.99	0.0919	0.0162
0.02	0.8	3.74	0.2	13.71	8.51	82.62	0.0970	0.0204
0.04	0.81	3.65	0.19	13.34	8.12	80.61	0.0992	0.0238

0.1	0.81	3.57	0.19	13.18	8.01	79.04	0.0986	0.0261
0.2	0.82	3.45	0.18	12.97	7.75	66.15	0.0853	0.0436
0.3	0.82	3.17	0.18	12.76	7.66	55.92	0.0730	0.0575
0.4	0.83	2.63	0.17	11.73	6.97	42.21	0.0605	0.0829
0.5	0.84	2.49	0.16	11.51	6.71	29.24	0.0435	0.1054
0.6	0.84	1.99	0.16	9.45	5.53	13.22	0.0239	0.1569

Table S5: Estimation of two different surface chemistries based on CsPbBr$_3$ PNCs with the rate constant of hole transfer (K$_{ht}$).

Sample	Hole transfer constant (K$_{ht}$) ($\times$ 10^8 s^{-1})	Improvement
Amine free	6.96	2.79
Amine	2.5	1
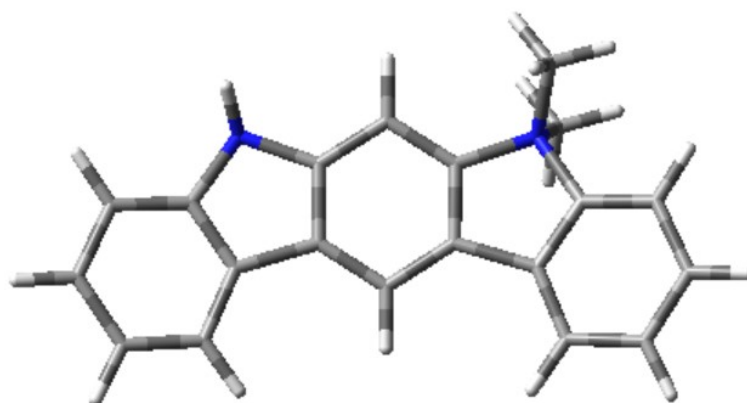
Figure S1. Optimized geometry of **SPS-Cbz** using B3LYP/6-311 g (d,p) level.
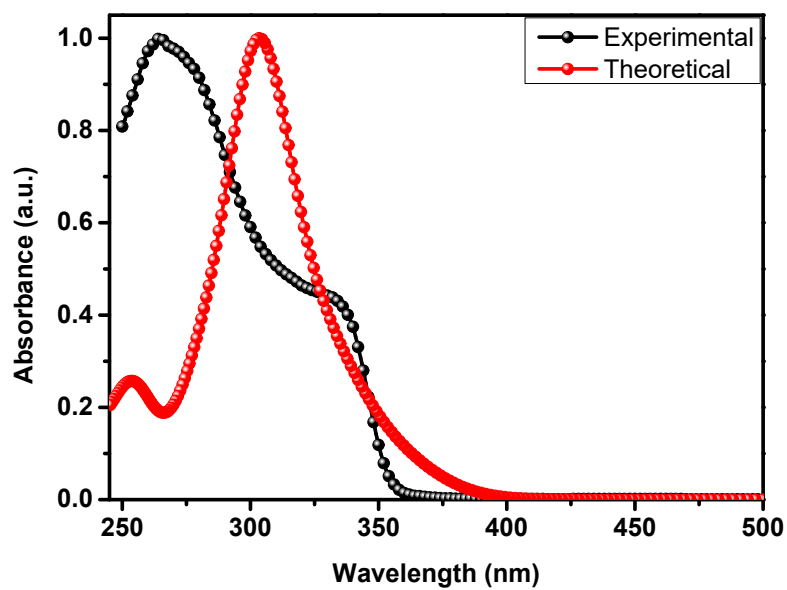
Figure S2. Simulated absorption of the SPS-Cbz in DCM solvent using B3LYP/6-311 g (d, p) level.
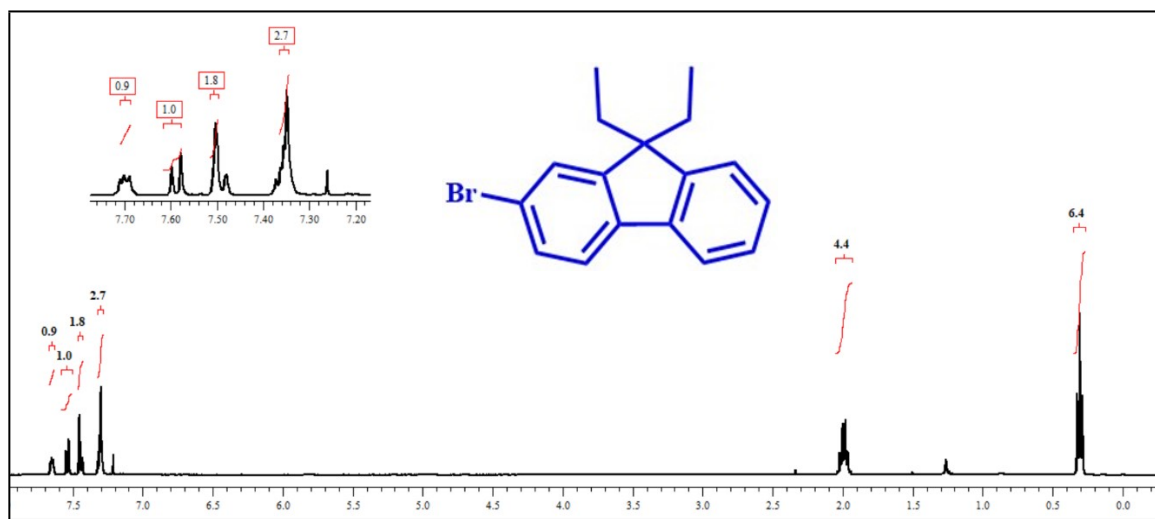
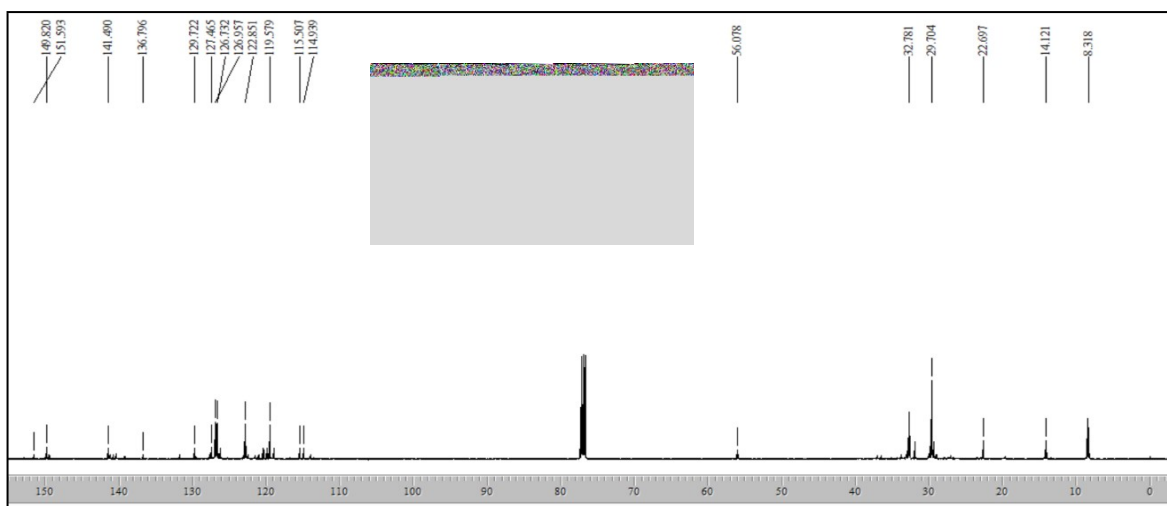## NMR Spectra

Figure S3. ^{1}H NMR spectra of Compound 1
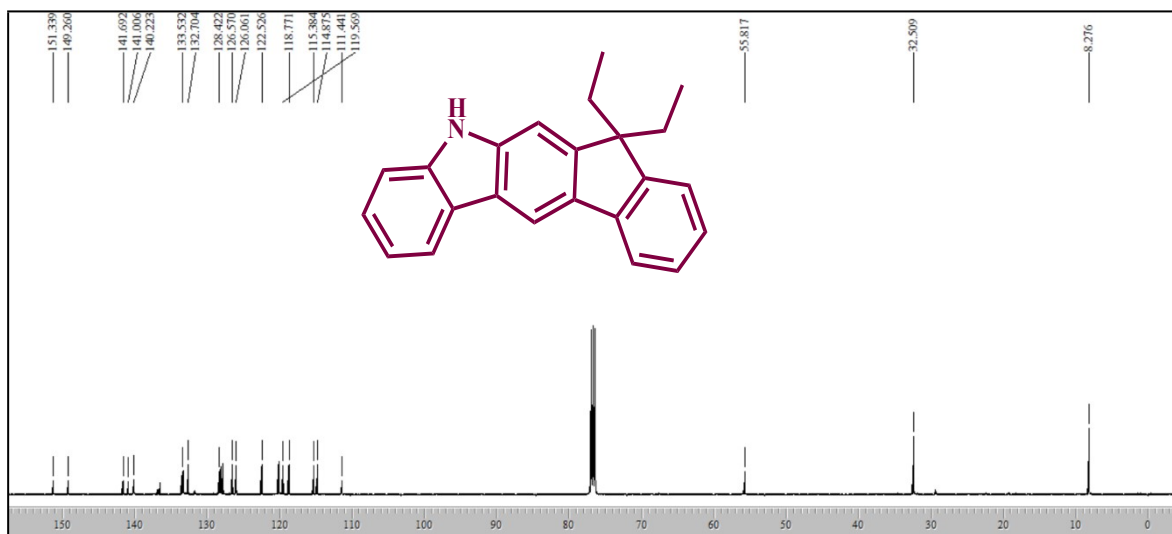
Figure S4. ^{13}C NMR spectra of Compound 1

Figure S5. ^{13}C NMR spectra of SPS-Cbz

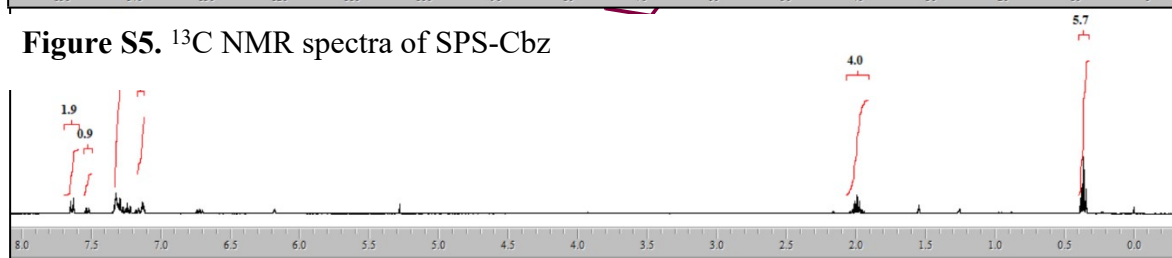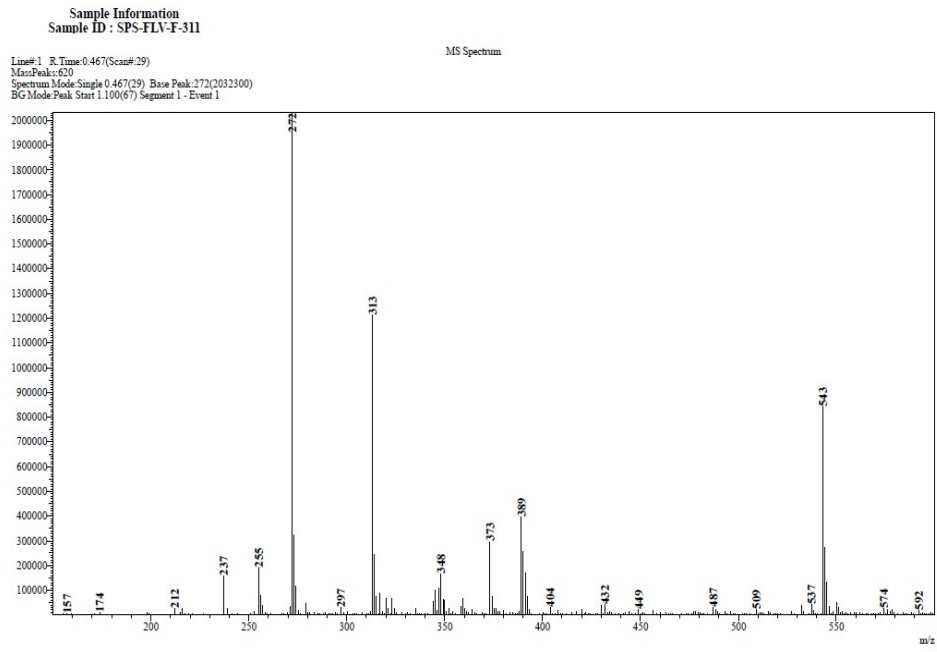**Figure S6.** ^{1}H NMR spectra of SPS-Cbz

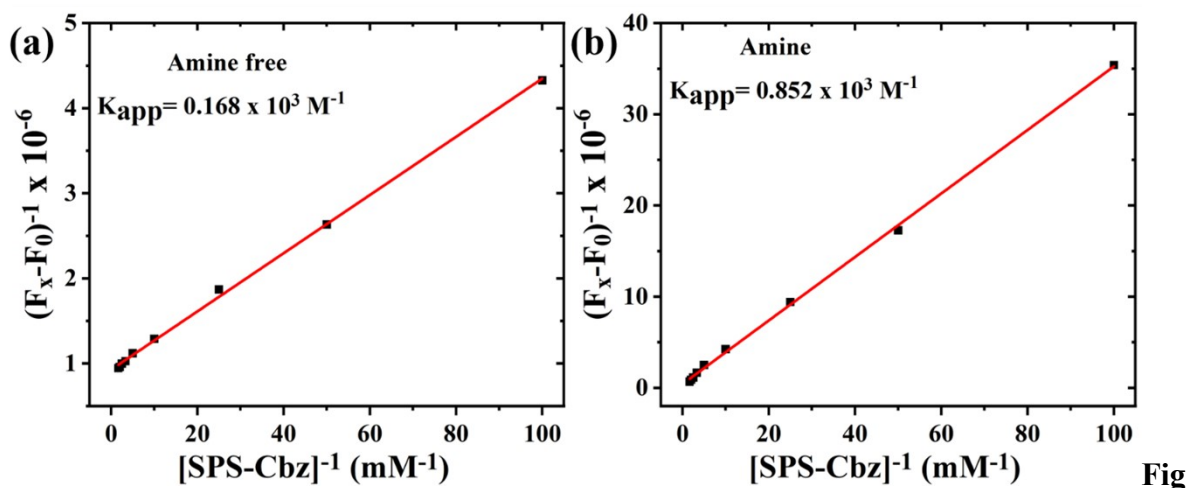**Figure S7.** Mass spectra of SPS-Cbz

Figure S8. Double reciprocal analysis fluorescence quenching data and apparent association constants (K_{app}) (a) Amine free and (b) Amine $CsPbBr_3$ PNCs respectively.

References

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