

**Supplementary Information:**

**Rapid microwave synthesis of fluorescent hydrophobic carbon dots**

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## **1. Experimental Section:**

### **1.1. Materials and Methods.**

Ortho-phosphoric acid, acetone, ethanol, chloroform, toluene, tetrahydrofuran, NMP, hexane, cyclohexane, dimethyl formamide and acetonitrile were purchased from Merck (India). Non-ionic surfactant polyoxyethylene-polyoxypropylene-polyoxyethylene (PEO-PPO-PEO) block co polymer pluronic F-68 (PF-68) was obtained from sigma Aldrich. All the chemicals were of analytical grade and used without further purification. Milli-Q grade water was used throughout the experiment.

### **1.2. Synthesis of hydrophobic carbon dots (HCDs).**

In a typical synthesis of hydrophobic carbon dots (HCDs), 60 mg of PF-68 was allowed to dissolve in 5 mL of water for about 15 minutes. To it 10 mL of o-phosphoric acid was added and the mixture was stirred for producing a homogeneous reaction mixture. The reaction mixture was then subjected to microwave irradiation in a domestic microwave oven for about 4 minutes at 450 watt; during this time period a brown colored product was obtained. The reaction mixture was allowed to cool down at room temperature and then to it 25 mL of water was added to obtain a brownish-black colored precipitate. Finally HCDs were extracted by using 25 mL of toluene. Similar procedure was repeated throughout except the extracting medium (chloroform) when HCDs were obtained in chloroform layer.

### **1.3. Dispersion of HCDs in organic medium.**

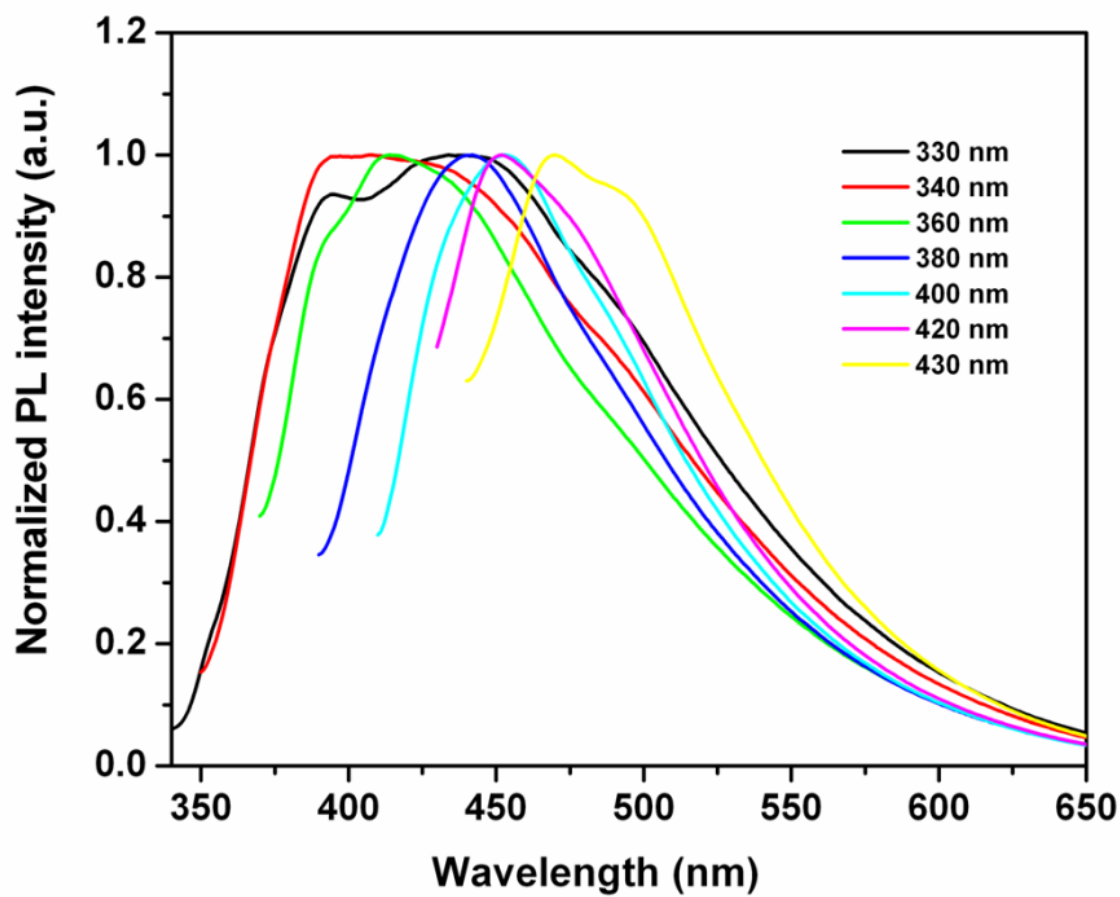
HCDs were synthesized by using the above mentioned method and extracted with 25 mL of toluene. Equal volume of HCDs extraction in toluene was taken in glass vials and then evaporated to dryness. To these pure HCDs about 2.5 mL of various organic solvents such as acetone, ethanol, chloroform, toluene, tetrahydrofuran, NMP, hexane, cyclohexane, dimethyl formamide and acetonitrile was added. The vial containing HCDs in organic solvent was mildly sonicated for 5 minutes and the resultant dispersion was kept under room temperature for dispersibility study.

### **1.4. Contact angle measurement of HCDs.**

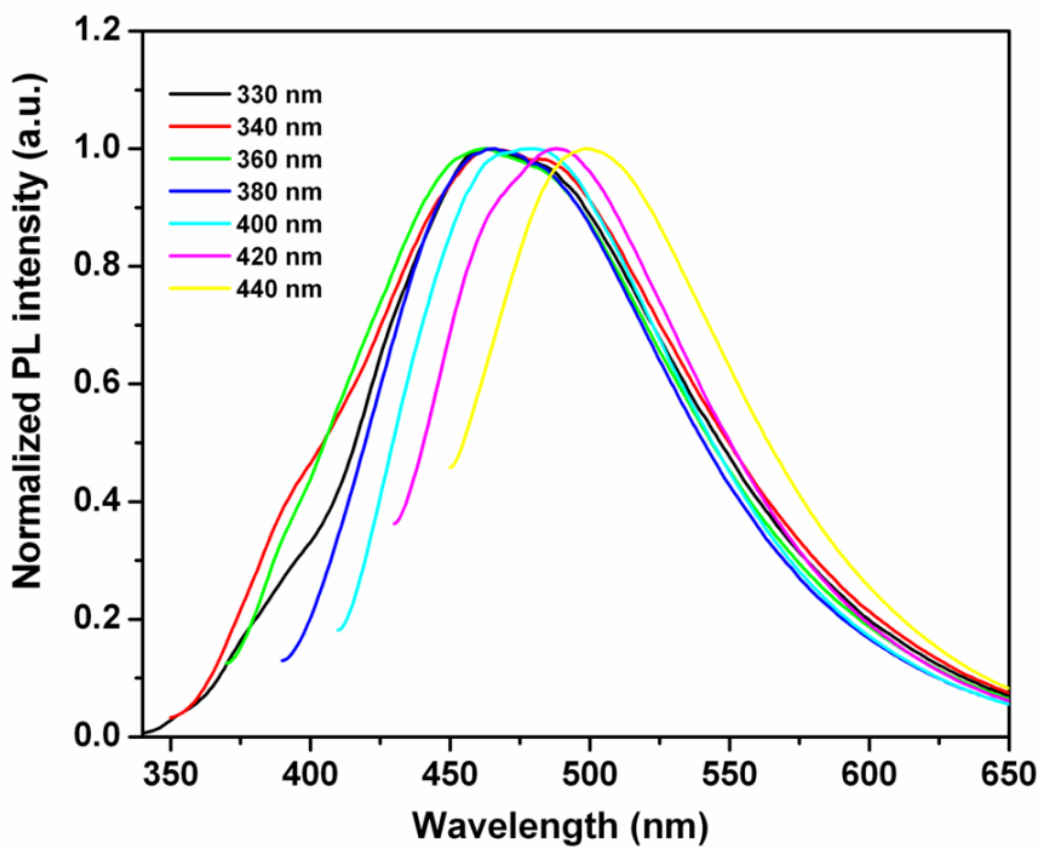
Water contact angle measurement was carried out on a glass slide by drop casting of HCDs dispersion. Prior to drop casting the glass slide was properly cleaned with piranha solution.

## 2. Characterizations:

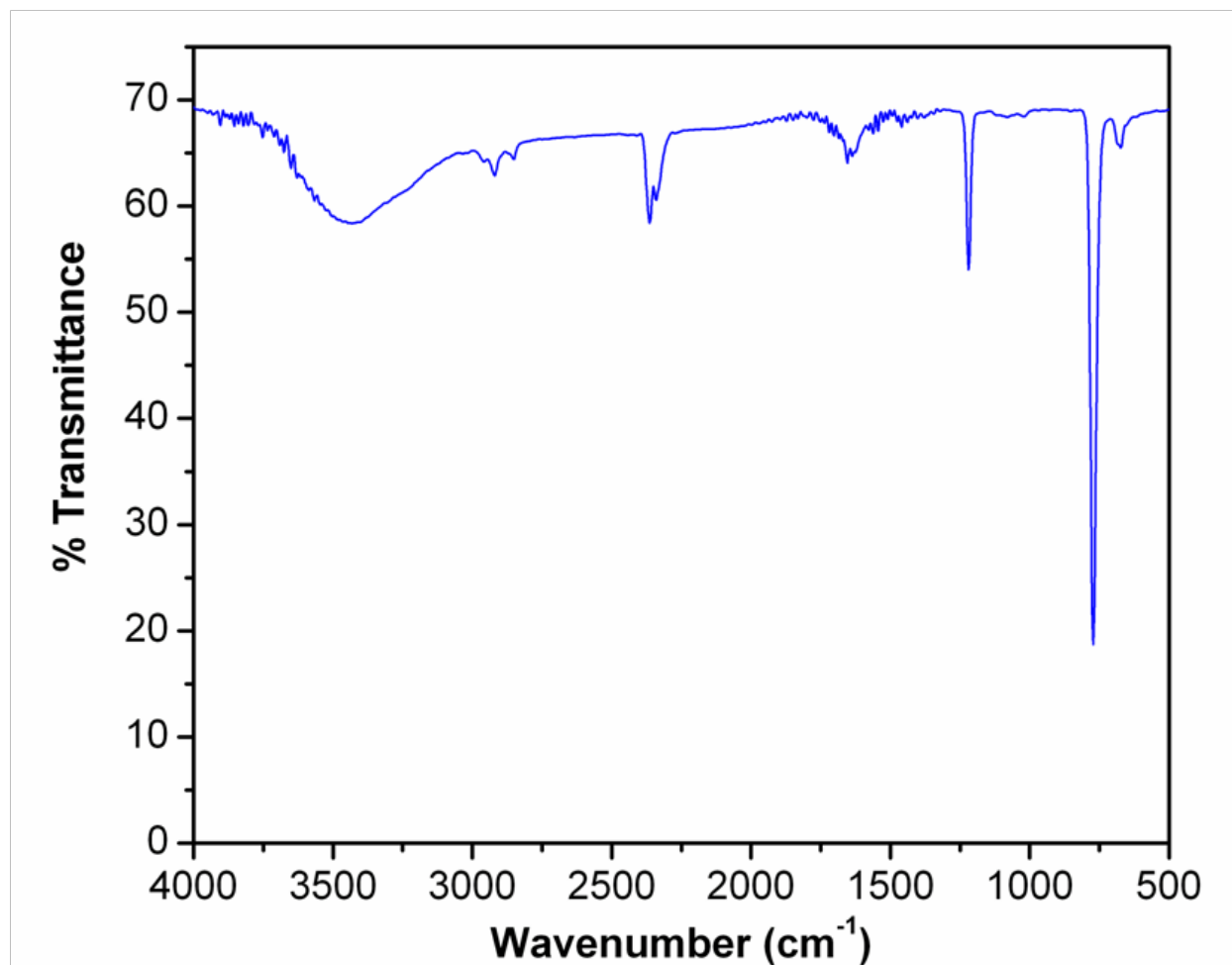
Fourier Transform Infrared Spectroscopy (FT-IR) was conducted by Perkin-Elmer spectrum RX-1 IR spectrophotometer by using methanolic dispersion of HCDs. For absorption and fluorescence measurements Shimadzu absorption spectrophotometer (model no: UV-1700) and Hitachi spectrofluorimeter (model no: F 7000) was used respectively; photostability and quantum yield was obtained by using the same spectrofluorimeter. Transmission electron microscopy (TEM) was carried out by using JEOL 2100, operating at an acceleration voltage of 200 kV. Surface topology of HCDs was obtained by using AFM (Veeco Metrology Inc.) in tapping mode. For AFM analysis toluene dispersion of the test sample was drop casted on a cleaned glass slide and dried in air. For TEM analysis a very dilute chloroform suspension was prepared, which was then deposited on a carbon coated copper grid and finally dried in air.  $^{31}\text{P}$  NMR spectrum was obtained by using Bruker Avance-II 400 MHz instrument operating at a frequency of 400 MHz using  $\text{CDCl}_3$  as the solvent. Phase characterization of the sample was carried out by using PANalytical xpert pro X-ray diffractometer with  $\text{Cu-K}\alpha$  -targets at 2mm slits. Time Correlated Single Photon Counting (TCSPC) lifetime measurement was carried out by using a picosecond diode laser at 370 nm (IBH, Nanoled) as a light source and the signal was taken at magic angle ( $54.7^\circ$ ) polarization using an Hamamatsu MCP PMT (3809U). The data analysis was evaluated by using IBH DAS, version 6, and decay analysis software. Fluorescence microscopic image was obtained by using Carl Zeiss-Axiolab fluorescence microscope. Meanwhile contact angle measurement was carried out in a glass slide using Digidrop automated contact angle measurement instrument.



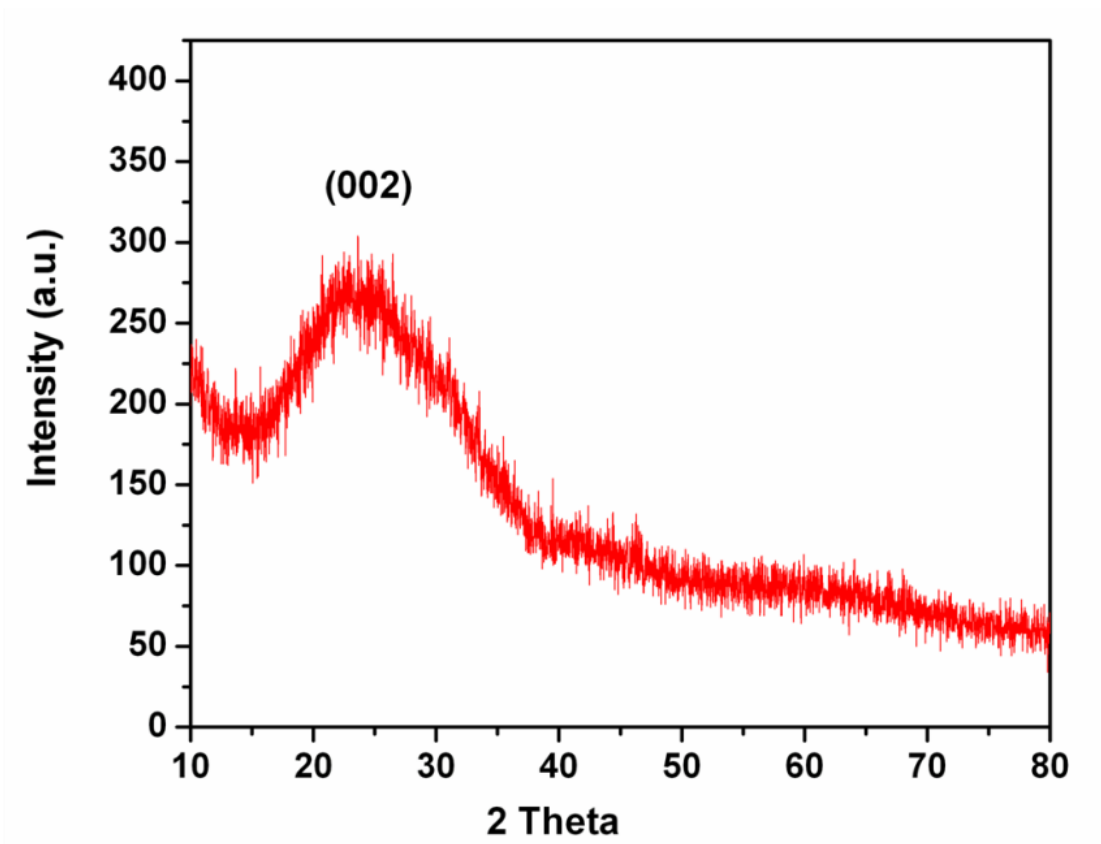
**Figure S1.** Normalized PL pattern of HCDs in toluene.



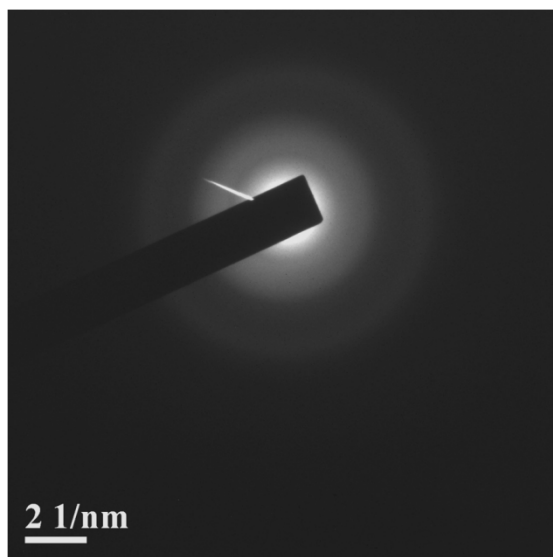
**Figure S2.** Normalized PL pattern of HCDs in chloroform.



**Figure S3.** FTIR spectra of HCDs.

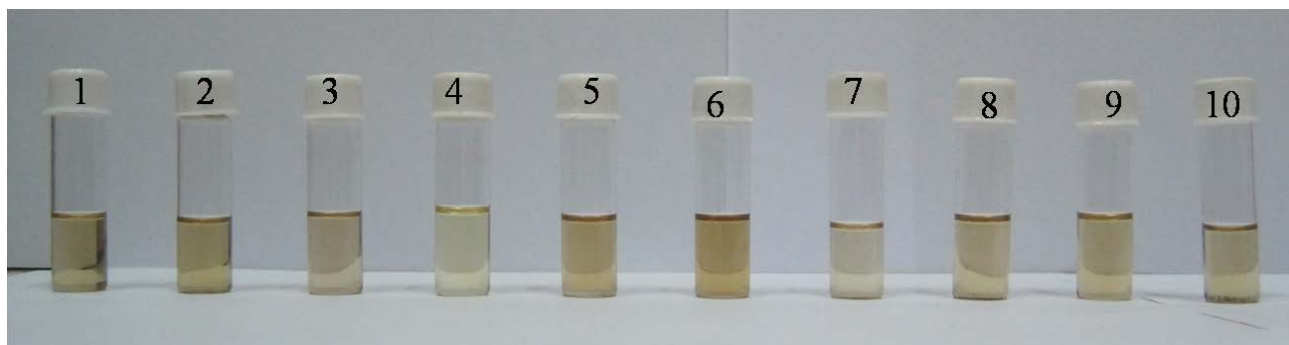


**Figure S4.** X-ray diffraction (XRD) pattern of HCDs.

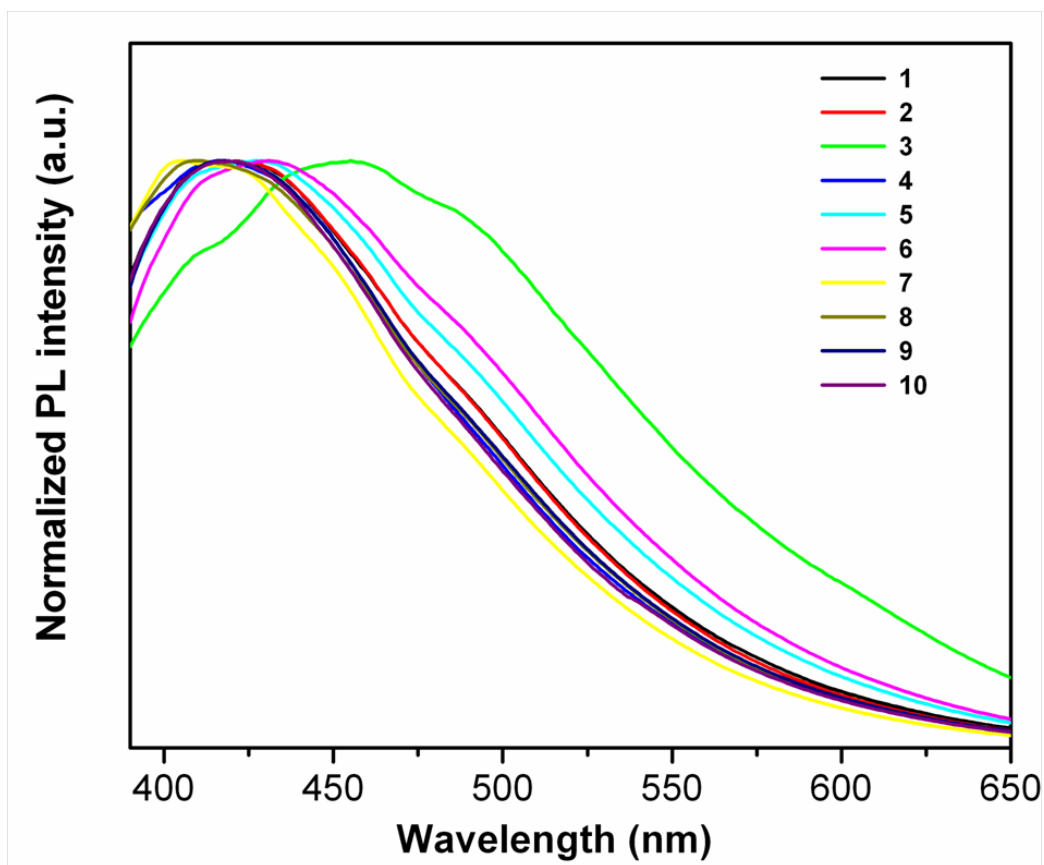


**Figure S5.** Selected area electron diffraction (SAED) pattern of HCDs.





**Figure S6.** Digital image displaying the dispersional stability of HCDs in different organic solvent. From left to right (1) Acetone, (2) Ethanol, (3) Chloroform, (4) Toluene, (5) Tetrahydrofuran, (6) N-Methyl-2-pyrrolidone (NMP), (7) Hexane, (8) Cyclohexane, (9) Dimethyl formamide (DMF), (10) Acetonitrile. HCDs exhibited stable dispersion even after 72 hours, only mild precipitation is observed in acetonitrile (10) at the bottom of the vial after long time.



**Figure S7.** Normalized PL spectra of HCDs in different organic solvents(1) Acetone, (2) Ethanol, (3) Chloroform, (4)Toluene, (5) Tetrahydrofuran, (6) N-Methyl-2-pyrrolidone (NMP), (7) Hexane, (8) Cyclohexane, (9) Dimethyl formamide (DMF), (10) Acetonitrile.

**Table 1.** Literature review of Hydrophobic/ organophilic carbon dots and their fabrication methods.

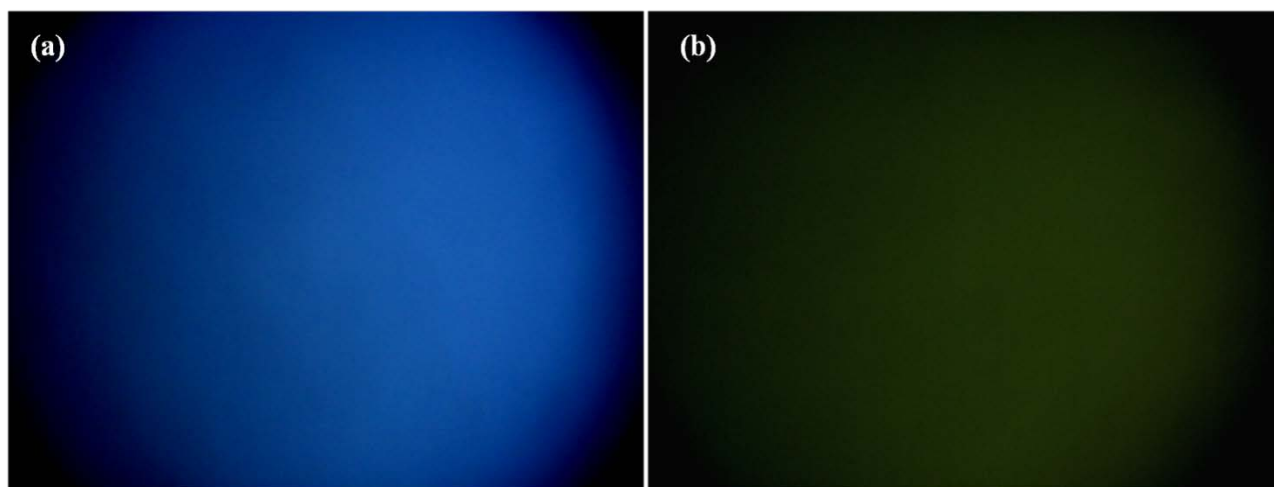
SL No.	Precursors	Method	Reference
1	Citric acid, 11-aminoundecanoate	Thermal decomposition	Chem. Mater., 2008, 20, 4539-4541.
2	Octadecyl ammonium citrate	Calcination	Small, 2008, 4, 455-458.
3	Citric acid, HDA	Hot injection method	Chem. Mater., 2010, 22, 4528-4530.
4	Citric acid, AEAPMS	Hot injection method	Adv. Funct. Mater., 2011, 21, 1027-1031.
5	Toluene, xylene, benzene	Confined combustion	Carbon, 2012, 50, 1298-1302.
<b>6</b>	<b>PF-68</b>	<b>Microwave pyrolysis</b>	<b>This work</b>

HDA: Hexadecyl amine.

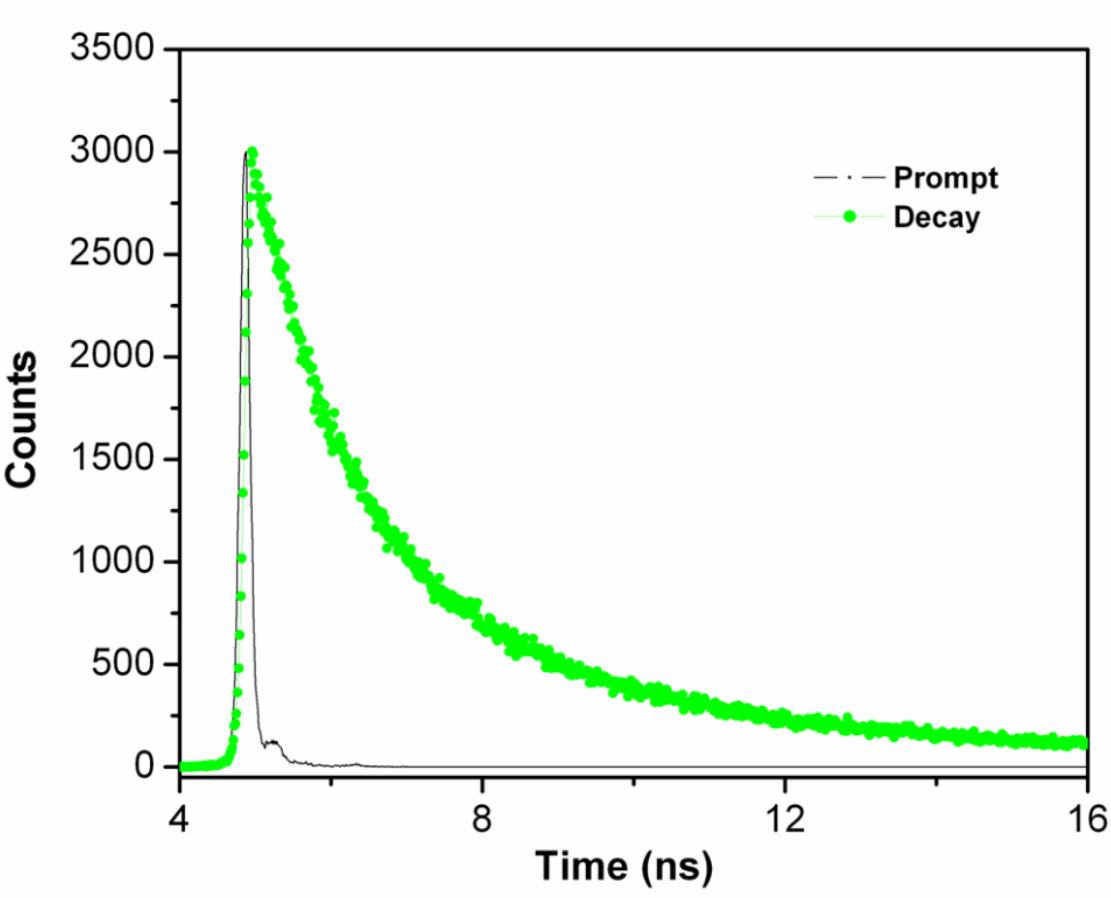
AEAPMS: *N*-( $\beta$ -aminoethyl)- $\gamma$ -aminopropyl methyldimethoxysilane.

PF-68: Pluronic F-68.

In the above mentioned synthetic procedure SL 5 work and this study was significantly different from all the above mentioned work. From SL1 to SL 4 work the inherent strategy was same; similar precursor (citric acid or citrate) first produced the carbon core followed by hydrophobic functionalization with long chain amines either by hot injection or by calcination/thermal decomposition method. Quantum yield was high when external passivating agent was used (long chain amines used in SL 3 and SL 4); else it was found to be moderate (SL 5, this work) or low (SL 1, SL 2). Meanwhile this study represented a simple single step microwave assisted technique to produce hydrophobic carbon dots from a unique non ionic surfactant which can produce the carbon centre as well as induce hydrophobic property. This process could be reproduced easily in comparison to SL 5 work where it was difficult to control the combustion reaction of volatile organic component leading to large fumes and uncontrolled reaction.



**Figure S8.** Fluorescence microscopic image of HCDs exhibiting (a) blue fluorescence and (b) green fluorescence at different excitation wavelength.



**Figure S9.** TCSPC lifetime profile of HCDs.

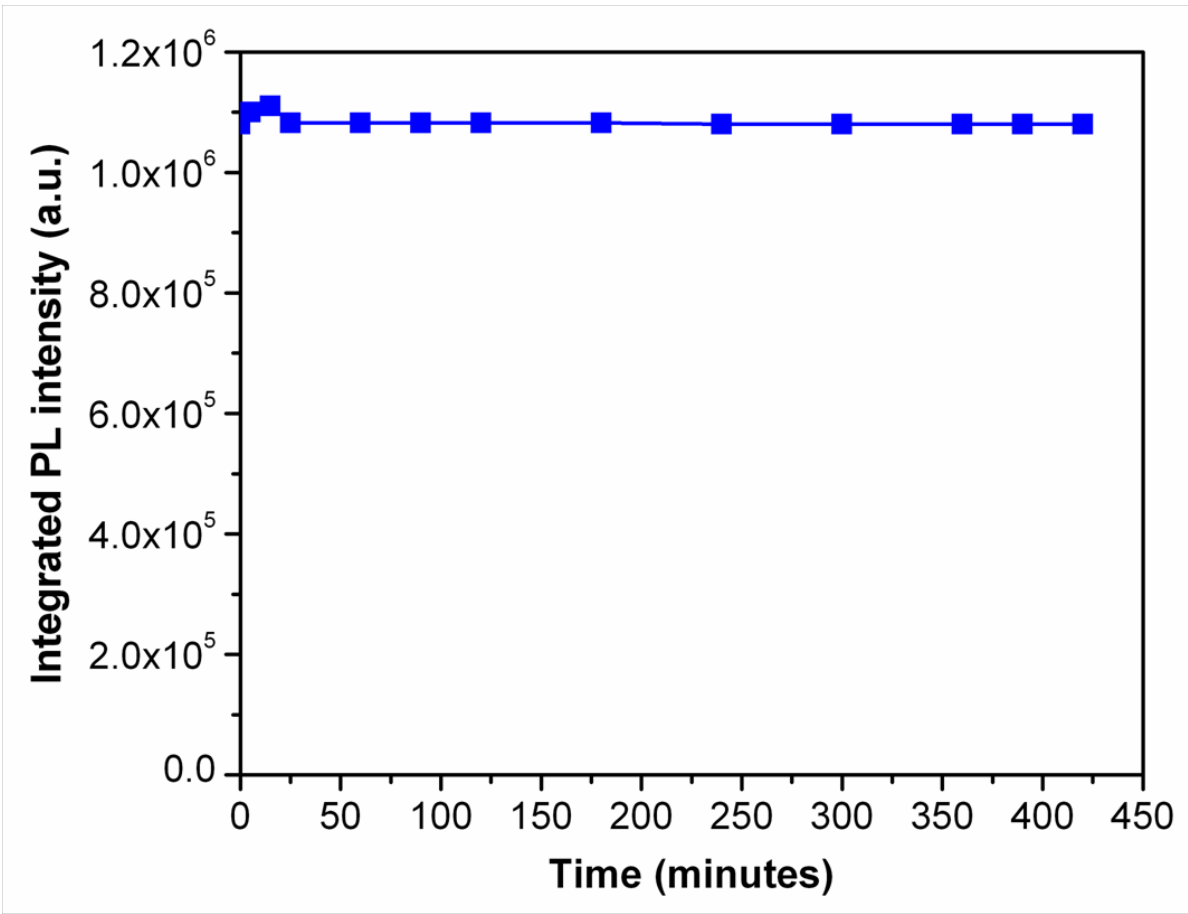
**Table 2.** Tabular representation of TCSPC lifetime measurements

Substance	a <sub>1</sub>	τ <sub>1</sub> (ns)	a <sub>2</sub>	τ <sub>2</sub> (ns)	a <sub>3</sub>	τ <sub>3</sub> (ns)	< τ > (ns)	χ <sup>2</sup>
HCDs	0.464	2.19	0.424	0.61	0.111	7.718	2.13	0.96

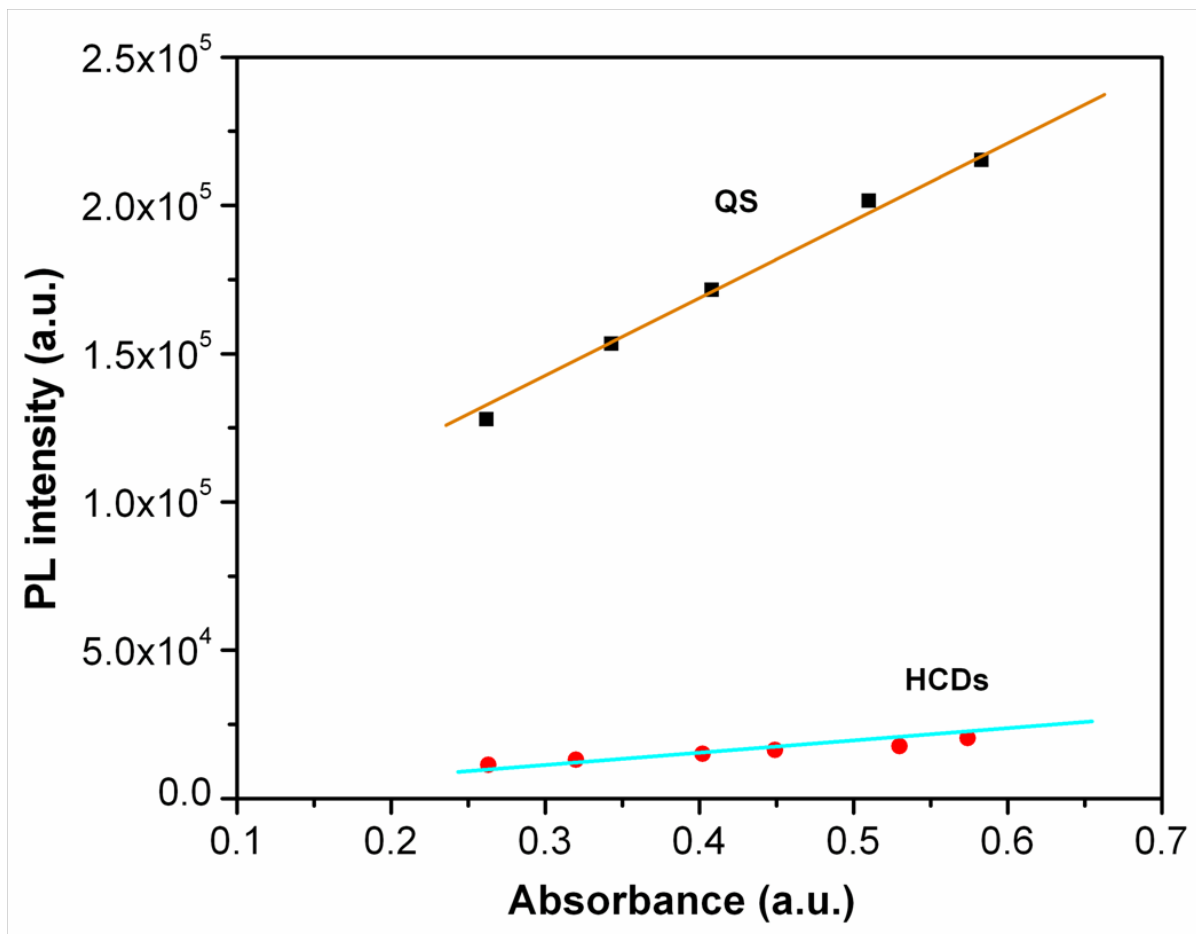
Average lifetime was calculated with the help of the following equation:

$$\tau_{av} = a_1\tau_1 + a_2\tau_2 + a_3\tau_3$$

where τ<sub>1</sub>, τ<sub>2</sub>, τ<sub>3</sub> were the first, second and third component of the decay time of HCDs and a<sub>1</sub>, a<sub>2</sub>, a<sub>3</sub> were the corresponding relative weightings of these components respectively.



**Figure S10.** Photostability measurement profile of HCDs against time (minutes).



**Figure S11.** Measurement of quantum yield of quinine sulphate (QS) and hydrophobic carbon dots (HCDs); displaying plot of integrated PL intensity against different absorbances.



Quantum yield of HCD was calculated by measuring the integrated PL intensity in toluene medium (refractive index  $\eta_T = 1.497$ ) against quinine sulphate in 0.1(M)  $H_2SO_4$  (refractive index  $\eta_W = 1.33$ ) as the standard of known quantum yield 54% using the following formula.

$$\Phi_{HCD} = \Phi_{QS} \times (I_{HCD}/I_{QS}) \times (\eta_T^2 / \eta_W^2)$$

Where  $\Phi$ ,  $I$  and  $\eta$  represented the quantum yield, slope of integrated PL intensity and refractive index respectively. The suffix QS and HCD denoted quinine sulphate and hydrophobic carbon dots (HCDs) respectively.

**Table T3.** Tabular representation of quantum yield measurements.

Substrate	Slope of integrated PL intensity	Refractive index	Quantum yield
Quinine sulphate	383143.51	1.33	54%
HCDs	39669.35	1.497	x

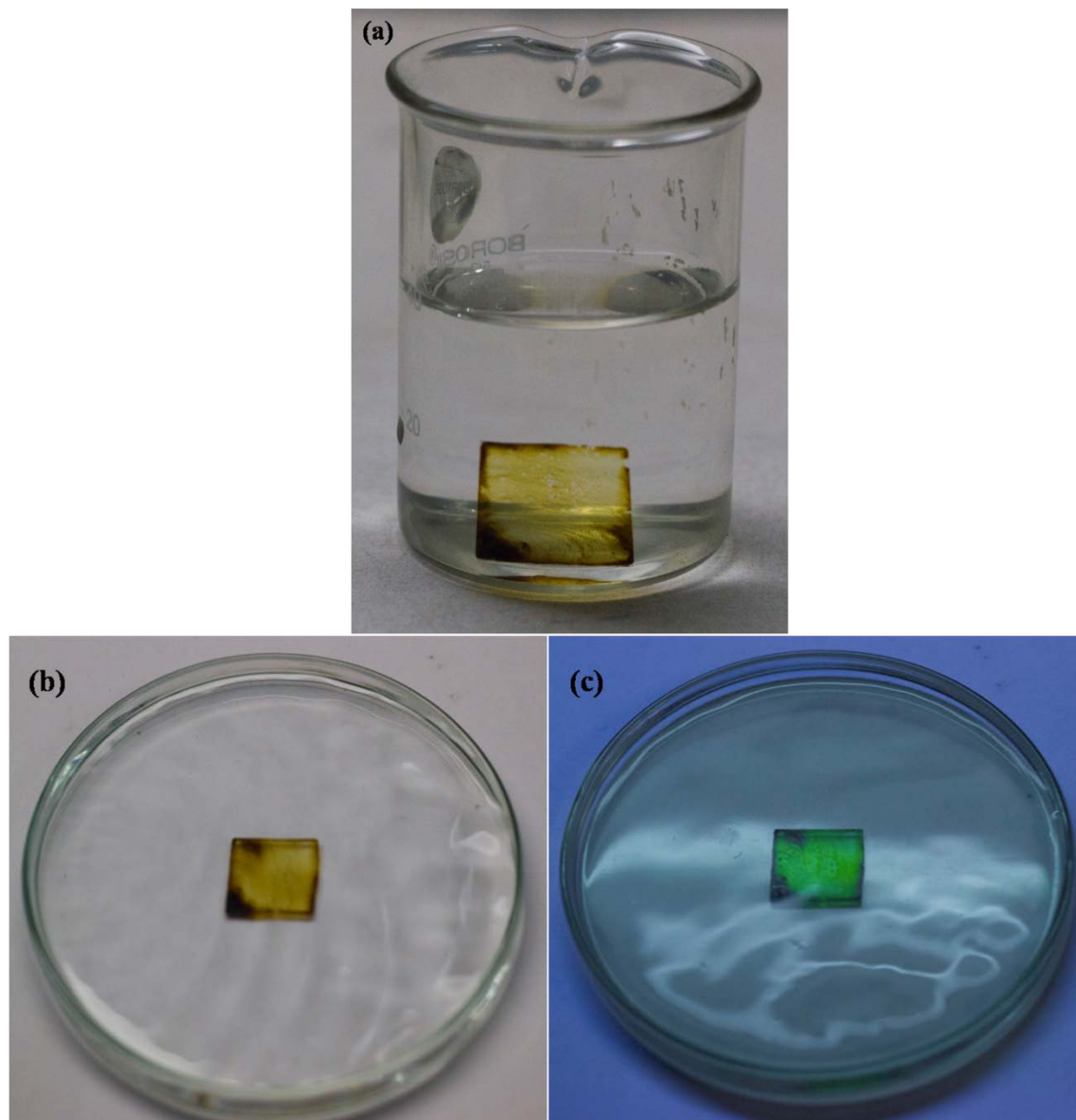
$$\Phi_{HCD}(x) = 54 \times (39669.35/383143.51) \times (1.497^2/1.33^2) \%$$

$$= 7 \%$$

Water droplets in glass slide appeared to be quasi spherical in nature; at the same time the droplet was symmetrical in nature. Water contact angle measurements was carried out thrice where average contact angle and the corresponding left and right contact angle are summarized in the following table T3.

**Table T4.** Measurements of water contact angle.

No. of repetition	Left contact angle (°)	Right contact angle(°)	Average contact angle (°)
1	121.7	121.7	121.7
2	121.4	120.9	121.2
3	122.8	122.3	122.6



**Figure S12.** (a) A clean glass slide drop casted with HCDs was kept in a beaker containing distilled water, HCDs treated glass slide was exceptionally stable under water for long time. No significant change was observed in the HCDs treated glass slide even after 10 days without getting wipe out in presence of water illustrating its water resistant property; (b) HCDs treated glass slide in normal light when kept in a Petri plate containing water exhibiting yellowish color; (c) HCDs treated glass slide in UV light when kept in a Petri plate containing water exhibiting green color. Normal yellow color and green fluorescence under UV light was restored in HCDs treated glass slide even in presence of water turmoil without getting wipe out from the glass slide. This unique water resistance ability of HCDs due to hydrophobic property together with high fluorescent property (without photobleaching) could be used in surface applications such as formulation of nano paints.