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SUPPORTING INFORMATION

Electronic compensation induced carbon dots@ PMMA with improved stability under UV aging

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Experimental

2.1 *Materials*

Methl Methacrylate (MMA), benzoyl peroxide, citric acid (CA) monohydrate (>99.5%) and C60 (99.9%) were purchased from Aladdin-reagent Ltd (Shanghai, China). Reagent-grade ammonium bicarbonate, trisodium citrate dehydrate, aqueous ammonia (AA), dodecylamine (DDA), ethanol, methanol, and methylbenzene (MB) were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All the materials are used as received without further treatment. Dialysis tube (Intercept molecular weight equals to 1000, 0.05% sodium azide) was purchased from Spectrumlabs (USA), which was washed three times with deionized water before using. Teflon lined stainless steel autoclave was obtained from Shanghai Yuan Huai Chemical Technology Co., Ltd., in which the chamber and shell materials are high quality polytetrafluoroethylene and stainless steel. The operation temperature and pressure are designed as 220 ^{o}C and 6 MPa, respectively.

2.2 *Sample preparations*

2.2.1 *Synthesis of functionalized oleophilic CDs (FOCDs)*

FOCDs were synthesized from MMA as single-source precursor as follows: MMA (5.30 ml) and DDA (2.97, 5.94, 11.88 and 17.82 ml) or $NH_3 \cdot H_2O$ (2 ml) in methylbenzene (20 ml) were sealed into the Teflon equipped stainless steel autoclave followed by hydrothermal reaction at various temperatures (180, 200 and 220 ^{o}C) for 4 h. The visual appearance of the final mixture reaction indicated oleophilic nanoparticles and the presence of oleophilic residues. These products were subjected to a purification procedure in order to remove both DDA and the residual MMA. Thus, each product was washed with deionized water (20 ml) and ethanol (20 ml), obtaining an emulsion, and centrifuged (10000 rpm) to separate and remove the below solution. The above procedures were repeated twice. Then deionized water (20 ml) was added to wash the product twice. This resulting product was further dialyzed for 24 h and evaporated remain solvent.

2.2.2 *Synthesis of non-functionalized oleophilic carbon dots (n-FOCDs)*

Typically, sodium citrate (0.2 g), NH_4HCO_3 (1.5 g) and deionized water (10 ml) were sealed into a Teflon equipped stainless steel autoclave (100 ml) followed by hydrothermal reaction at 180 ^{o}C for 4 h. Dry CDs were obtained by dialysis for 24 h through a dialysis tube (molecular weight cutoff, 1000 Da) and evaporation of the remaining water. Then oleophilic CDs (5 ml) were dispersed in deionized water (15 ml) and the pH was tuned to 5~7 using ethylic acid. Methylbenzene (MB, 20 ml) and dodecylamine (DDA, 0.1 g) were added to the system. The mixed suspension was transferred to a 100 ml Teflon-lined autoclave and heated at 160 ^{o}C for 4 h. Then the upper solution was removed and centrifuged 3 times with distilled water. Finally, the *n*-FOCDs were obtained by evaporating the remaining methylbenzene.

2.2.3 *Fabrication of C60, n-FOCDs and FOCDs@ PMMA*

0.068 g C60, 1 ml as-synthesized *n*-FOCDs (~0.38 g) and FOCDs (~0.38 g) solution was dried in vacuum oven for about 4 h at room temperature, followed by the addition of MMA (12 ml) and benzoyl peroxide (BPO, 0.03 g) to initiate polymerization. Note that the mass percent of C60, *n*-FOCDs and FOCDs in PMMA is about 0.6 %, 3.3 % and 3.3 %, respectively. The reaction was kept for about 60 min at 85 °C in water bath, then poured into a plastic box (r=14 mm; h=13 mm) for further polymerization at 60 °C for 48 h, finally polished into a circular block (Φ= 24×2.2 mm).

2.3 *UV aging*

UV aging was performed in SGS-CSTC Standards Technical Services (Shanghai) Co., Ltd. according to the American society for Testing and Materials (ASTM) G154-12a. The exposure cycle was: Lamp type: UVA-340; 8 h UV at (60±3) °C BPT, 0.89 $W/(m^2 \cdot nm^{-1})$@340 nm; 4 h condensation at (50±3) °C BPT. Note that the as-fabricated circular blocks were divided into four quarters to undergo UV aging.

2.4 *Characterizations*

The particle diameter was examined with a JEM-2100F transmission electron microscope (TEM, JEOL Co. Ltd.) operating at 200 kV. A drop of corresponding carbon dot solution (aqueous and ethanol solution for *n*-FOCDs and FOCDs, respectively.) was loaded on a copper grid with amorphous ultrathin carbon film and was left to dry before transferring into the TEM sample chamber. Raman spectra were recorded on a confocal microprobe Raman spectroscopy (Renishaw InVia) with an excitation wavelength of 633 nm at a laser power of 10 mW. Fourier Transform Attenuated Total Reflection Infrared Spectroscopy (FT-ATR-IR) was performed on a FT-IR spectrometer with 8 nm step size and 32 scanning times (Nicolet iS50). X-ray photoelectron spectroscopy (XPS) measurements were carried on an X-ray photoelectron spectrometer (Thermo-VG Scientific ESCALAB 250) using a monochromated Al K_α (1,486.6 eV) X-ray source. The transmittance spectra of as-fabrication composites were performed from a UV-vis-NIR spectrophotometer (Cary 5000). Photoluminescence spectra were performed using spectrometer (Hitachi F-4600). The scan speed was fixed at 240 nm/min, the voltage was 700 V and the slits were fixed at 2.5 nm. ^1H NMR spectra of the samples were recorded with Varian Unity Plus 500 system spectrometer with D_2O as solvent.

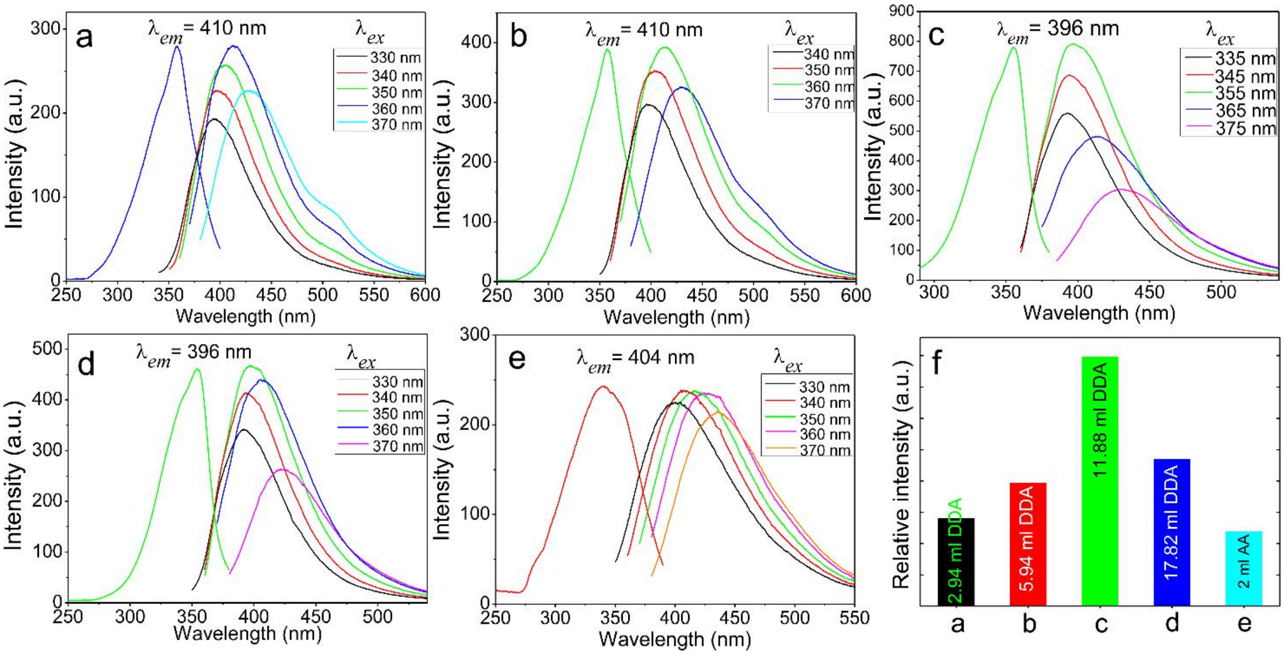

Fig. S1. (a-e) Photoluminescence spectra of the as-synthesized FOCDs processed at 220 ^{o}C for 4 h with 2.94, 5.94, 11.88 and 17.82 ml DDA, and 2 ml AA instead of DDA. The emission spectra show excitation-wavelength dependence. (f) Histogram of emission intensity comparison of these products. In the view of emission intensity, the optimal ratio of reactants are determined as V(MMA): V(DDA) = 5.33: 11.84, equivalently C (MMA): N (DDA)=1. When ammonia (AA) has been used to replace DDA as the reactant, the luminescence intensity of the resultant is much weaker compared to that of DDA existing

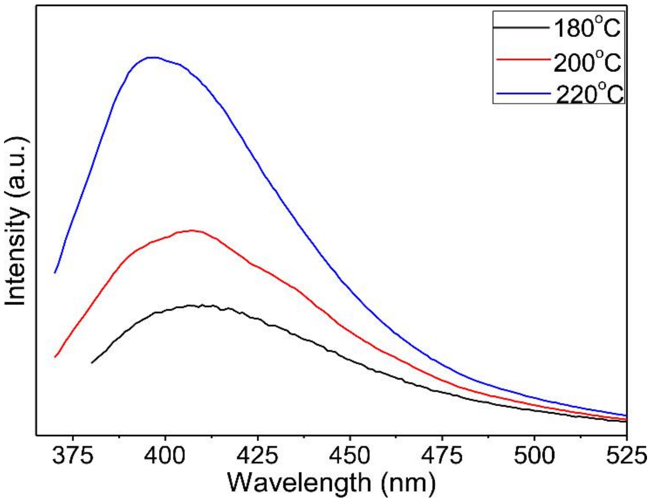

Fig. S2. Emission intensity of the as-prepared FOCDs with MMA, DDA and MB under 180, 200 and 220 ºC, respectively. Note that 220 ºC was employed as the final reaction temperature considering the experimental safety although elevatory temperature gives rise to persistent increasing in luminesence intensity

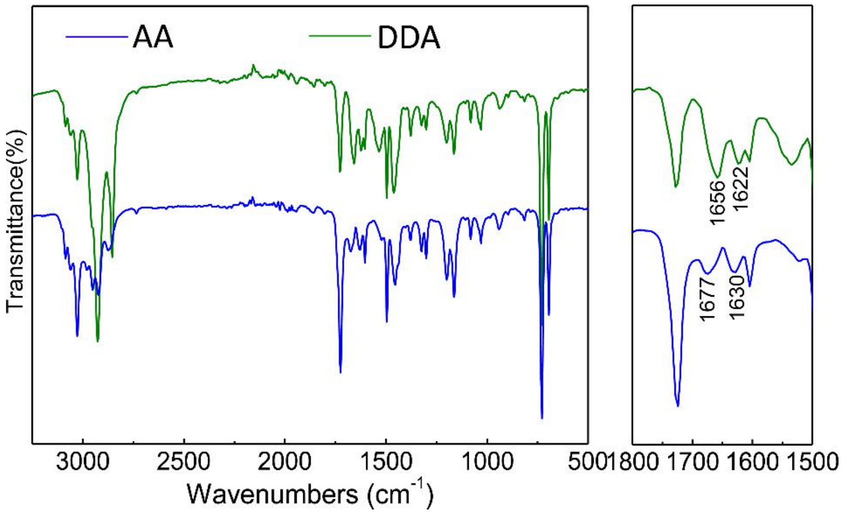

Fig. S3. FT-ATR-IR spectra of the products when reactants consist of DDA or AA. The amplified region from 1500-1800 cm^{-1} shows the formation of amide bond both under DDA and AA existence.

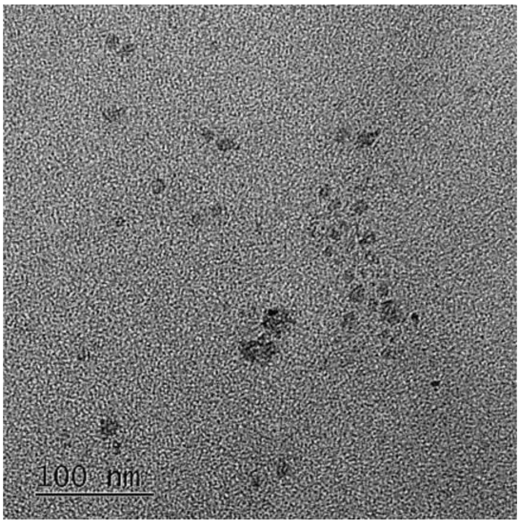

Fig. S4. TEM image of FOCDs produced from AA, MMA and MB. The reaction conditions are the same with that when DDA exists, while the size distribution is boarder and the mean size (10 -20 nm) is almost 2-4 times larger than that when DDA exists. The result shows AA could coarsen the carbon particles with a broad size distribution ranging from 10 to 20 nm, i.e. 2-4 times larger than that of existing. Thus, DDA play a vital role in ultrasmall FOCDs preparation due to its long fatly chain which can restrain agglomeration of FOCDs

Table S1. Quantitative elemental analysis of the as-prepared FOCDs based on the full-scan XPS spectrum.

Elements	FWHM (eV)	Area (Counts·eV)	Atomic (%)
C1s	1.13	49206.37	77.25
O1s	1.07	37148.26	20.49
N1s	1.05	2555.31	2.26

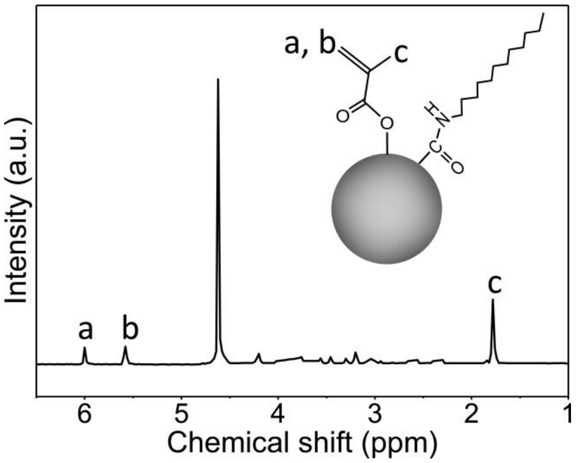

Fig. S5. ^{1}H NMR spectrum of FOCDs with D_2O as solvent.

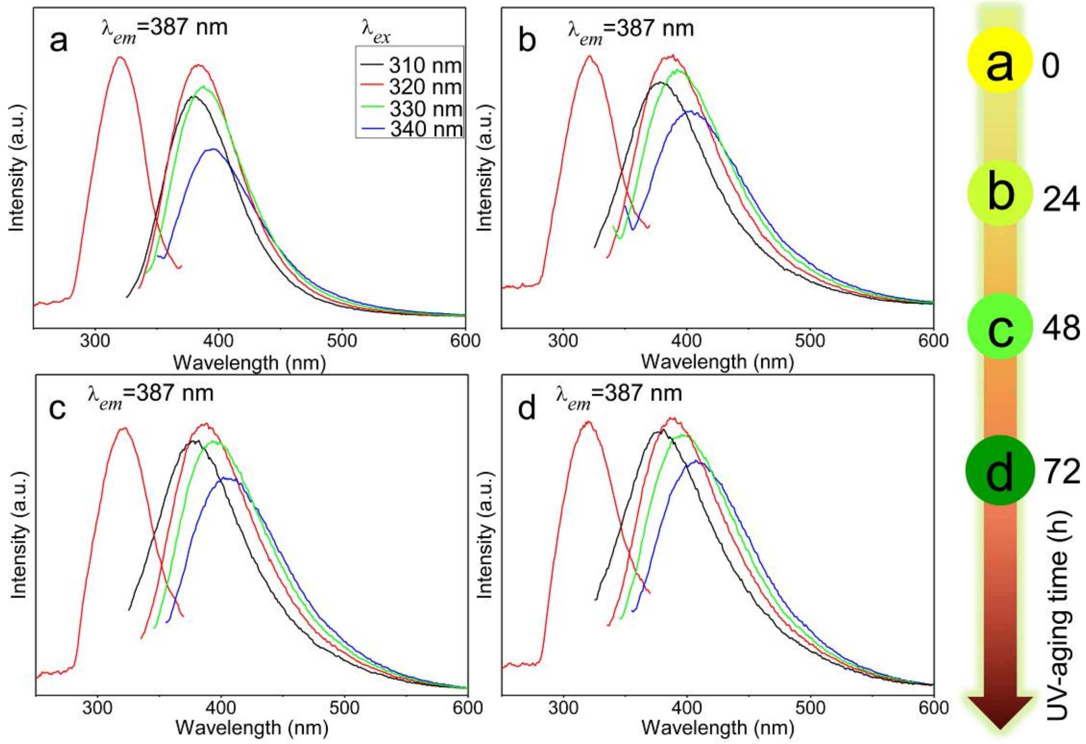

Fig. S6. Luminescence spectra of the as-fabricated FOCDs@ PMMA composite under (a) 0 h, (b) 24 h, (c) 48 h and (d) 72 h UV exposure. The emission spectra are tunable depending on excition wavelengths, and the optimal excition and emission wavelengths are determined as 320 and 387 nm

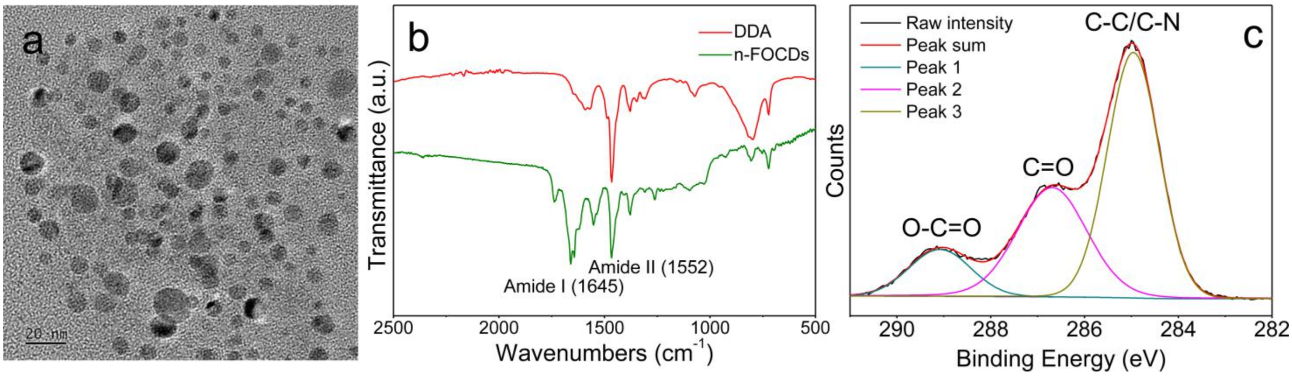

Fig. S7. (a) TEM image of *n*-FOCDs. (b) FT-ATR-IR spectrum of the as-prepared *n*-FOCDs, the spectrum of DDA is for comparison. The Amide I (1645 cm^{-1}) and Amide II (1552 cm^{-1}) shows the formation of amide bond. (c) High-resolution XPS spectrum of C1s, which indicates the existence of O-C=O, C=O and C-C/C-N without observed C=C

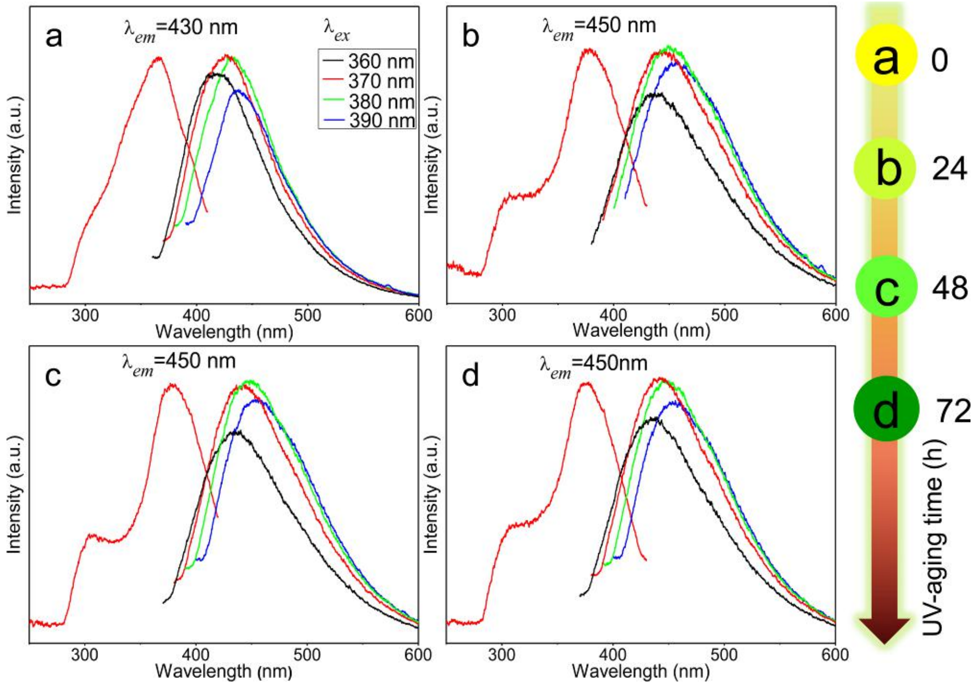

Fig. S8. Luminescence spectra of the as-fabricated *n*-FOCDs@ PMMA composite under (a) 0 h, (b) 24 h, (c) 48 h and (d) 72 h aging-test UV exposure. The optimal excition and emission wavelengths without aging are determined as 370 and 430 nm, and the optimal ones shift to 380 and 450 nm after UV-exposure, respectively

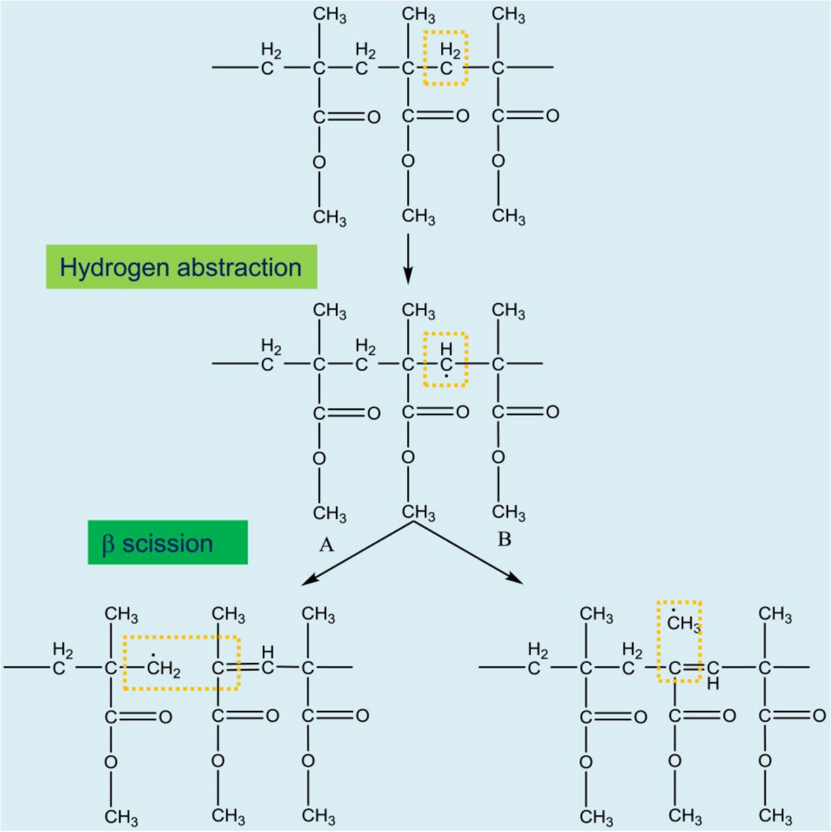

Fig. S9. UV-aging mechanism diagram of PMMA consisting of two stages: hydrogen abstraction and β scission

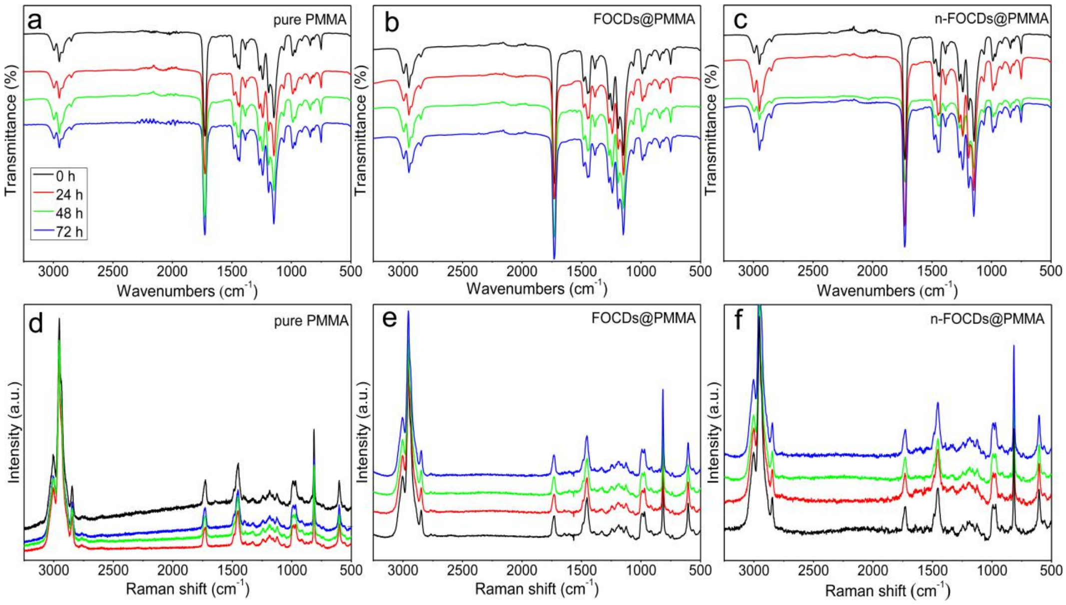

Fig. S10. FT-ATR-IR and Raman spectra of the pure PMMA (a, d), FOCDs@ PMMA (b, e) and *n*-FOCDs@ PMMA composites (c, f).

Table S2. Typical synthesis methods and proposed applications of oleophilic CDs

No.	Precursors	Methods	Application fields	References
1	Octadecylamine ammonium, citric acid	Calcination	No Given	[1]
2	Citric acid, 11-aminoundecanoate	Thermal decomposition	No Given	[2]
3	Citric acid, HDA	Hot injection method	No Given	[3]
4	EDTA-2Na, DDA	Thermal decomposition, solvothermal method	No Given	[4]
5	Acrylic acid, 1,2-ethanediamine	Microwave pyrolysis and Surface vinylation	No Given	[5]
6	Citric acid, AEAPMS	Hot injection method	bioimaging	[6]
7	PF-68	Microwave pyrolysis	No Given	[7]
8	AEAP-TMOS, citric acid	Hot injection method	Organic scintillators	[8]
9	PMA, 1-octadecene	Hot injection method	Sensing in Organic Media	[9]
10	Methyl methacrylate, dodecylamine	solvomethod	Anti-aging, luminescent probe	This work

HDA: 1-hexadecylamine
AEAPMS: N-(β-aminoethyl)-γ-aminopropyl methyl-dimethoxy silane
PMA: dodecyl-grafted poly (isobutylene-alt-maleic anhydride)
EDTA: Ethylene Diamine Tetraacetic acid
DDA: Dodecylamine
PF-68: Pluronic F-68
AEAP-TMOS: [3-(2-aminoethylamino)propyl]trimethoxysilane

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