Facile Functionalization of HTC-derived Carbon Microspheres

Supplemental Information

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Supporting Information

General. Both ^{1}H NMR spectra and ^{13}C NMR were taken on DPX-400 MHz Bruker instruments. NMR chemical shifts were reported as δ values in ppm relative to TMS or deutrated solvent: $CDCl_3$ (7.26). Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration and coupling constant(s) in Hz. Multiplets were reported over the range (in ppm) it appeared. Carbon NMR data were recorded relative to the following solvent signals: $CDCl_3$ (77.0). Elemental analysis was performed for carbon, hydrogen and nitrogen using a Vario EL Elemental Analyzer. Fourier-transform infrared (FT-IR) spectroscopy was done at room temperature with a BioRad 6000 FT-IR spectrometer equipped with a Single Reflection Diamond ATR. Scanning electron microscopy (SEM) pictures were taken with a GEMINI LEO 1550 microscope at 3 kV. Fluorescent images were taken using epi-fluorescence microscope Olympus BX 51 with a software Cell'P (Olympus, Germany) under UV light at excitation wavelength 361 nm. Following solvents were used without further purification; anhydrous DMF, anhydrous *p*-xylene, *o*-dichlorobenzene (all from Aldrich).

Materials. Glucose (Acros), maleimide, 9-anthracene methanol, acryloyl chloride (Aldrich), 4,5-dicyano-1,3-dithiol-2-one (TCI Europe), PEG480 acrylate (Aldrich), were used as received unless otherwise specified.

General procedure for functionalization of HTC@180 and @550. To carbonaceous material was added pre-determined amount of dienophile and a solvent. The reaction mixture was allowed to react for 48 h at 100 °C. The reaction mixture was the filtered, and the solid was washed repeatedly with hot THF and with acetone. The solid was then dried in vacuum oven at 80 °C overnight.

General procedure for the hydrolysis. Carbons from the previous step were refluxed in 0.25N HCl in ethanol for 48 h. The reaction was the filtered and the solid was washed with ethanol, water, and acetone. The solid was then dried in vacuum oven at 80 °C overnight.

General procedure for the conjugate addition of PEG acrylate onto thiol-functionalized carbons. To thiol-functionalized carbons suspended in THF was added an excess amount of the PEG acrylate and DIPEA. The reaction mixture was allowed to react for 48 h at room temperature. After 48 h, the reaction mixture was the filtered, and the solid was washed repeatedly with hot THF and with acetone. The solid was then dried in vacuum oven at 80 °C overnight.

Synthesis of anthracene acrylate. To 9-anthracenemethanol and DIPEA dissolved in anhydrous THF, acryloyl chloride was added dropwise at 0°C. The reaction was allowed to warm up to room temperature after 1 hr and was allowed to run overnight. The reaction mixture was condensed *in vacuo*, then CH_2Cl_2 was added and washed with 0.1N

HCl (x 2), aq. NaHCO3 (x 2), water (x 2), and finally with brine. The crude mixture was dried over $MgSO_4$, filtered, then was condensed *in vacuo*. The crude product was purified by column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.39 (d, *J* = 8 Hz, 2H), 8.06 (d, *J* = 8 Hz, 2H) 7.63-7.59 (m, 2H), 7.54 – 7.51 (m, 2H) 6.45 (dd, *J* = 17, 1.2 Hz, 1H) 6.27 (s, 2H), 6.17 (dd, *J* = 17, 12 Hz, 1H), 5.83 (dd, *J* = 12, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 131.4, 131.2, 129.3, 129.1, 128.3, 126.7, 126.1, 125.1, 126.0, 59.0

Table S1. Elemental Analysis found for tetracyanoethylene (TCNE), maleimide (MI), and maleic anhydride (MA) functionalized HTC@180 and @550.

Entry	Dienophile	HTC@	Temp	solvent	C%	H%	N%	S%
1	TCNE	180	50°C	DMF	57.7	3.6	10.3	0.1
2	TCNE	550	50°C	DMF	88.0	3.1	0.6	0.1
3	TCNE	550	75°C	DMF	83.2	3.2	1.6	0.0
4	TCNE	550	100°C	DMF	82.6	3.3	2.00	0.1
5	MI	180	100°C	DMF	61.8	4.2	2.7	0.1
6	MI	550	100°C	DMF	82.7	3.3	3.8	0.0
7	MA	180	90°C	DMF	59.3	4.2	0.2	0.0
8	MA	550	90°C	DMF	80.9	3.0	0.2	0.0

Scheme S1. Proposed reaction scheme of the alcoholysis and the subsequent conjugate addition

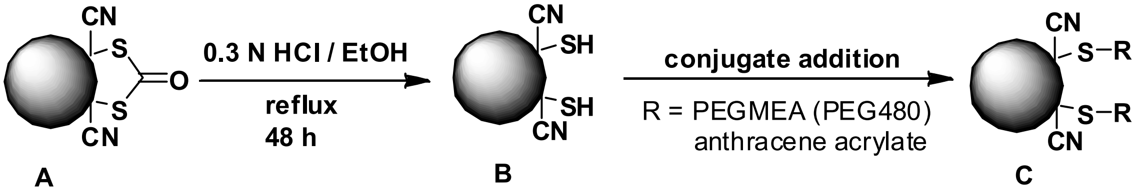

Table S2. Elemental Analysis found for HTC@180 and @550 after the hydrolysis (B) and after the conjugate addition of anthracene acrylate (C)

sample	C%	H%	N%	S%
B-180	57.9	3.7	4.3	8.1
C-180	58.5	3.9	4.3	7.3
B-550	82.9	2.8	1.0	1.6
C-550	82.6	2.9	1.2	1.7

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Supplemental Information – FT-IR, SEM, NMR, Fluorescence microscopy

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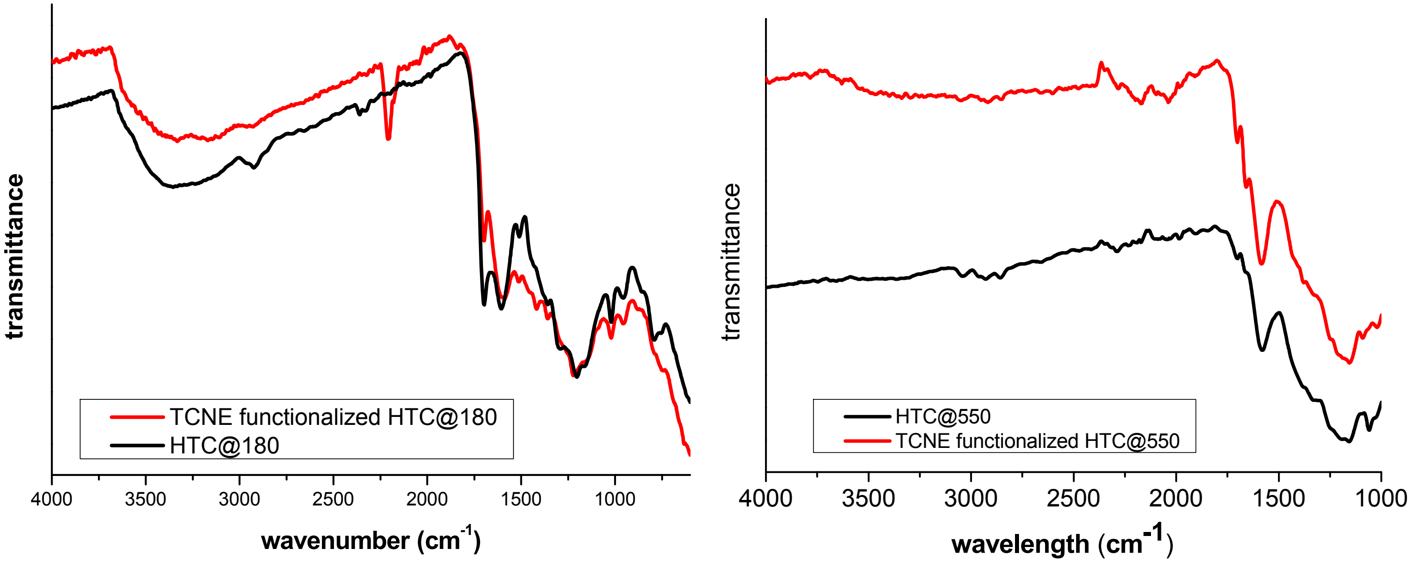


Figure S1. FTIR of tetracyanoethylene (TCNE)-functionalized HTC@180 (left) and 550 (right)

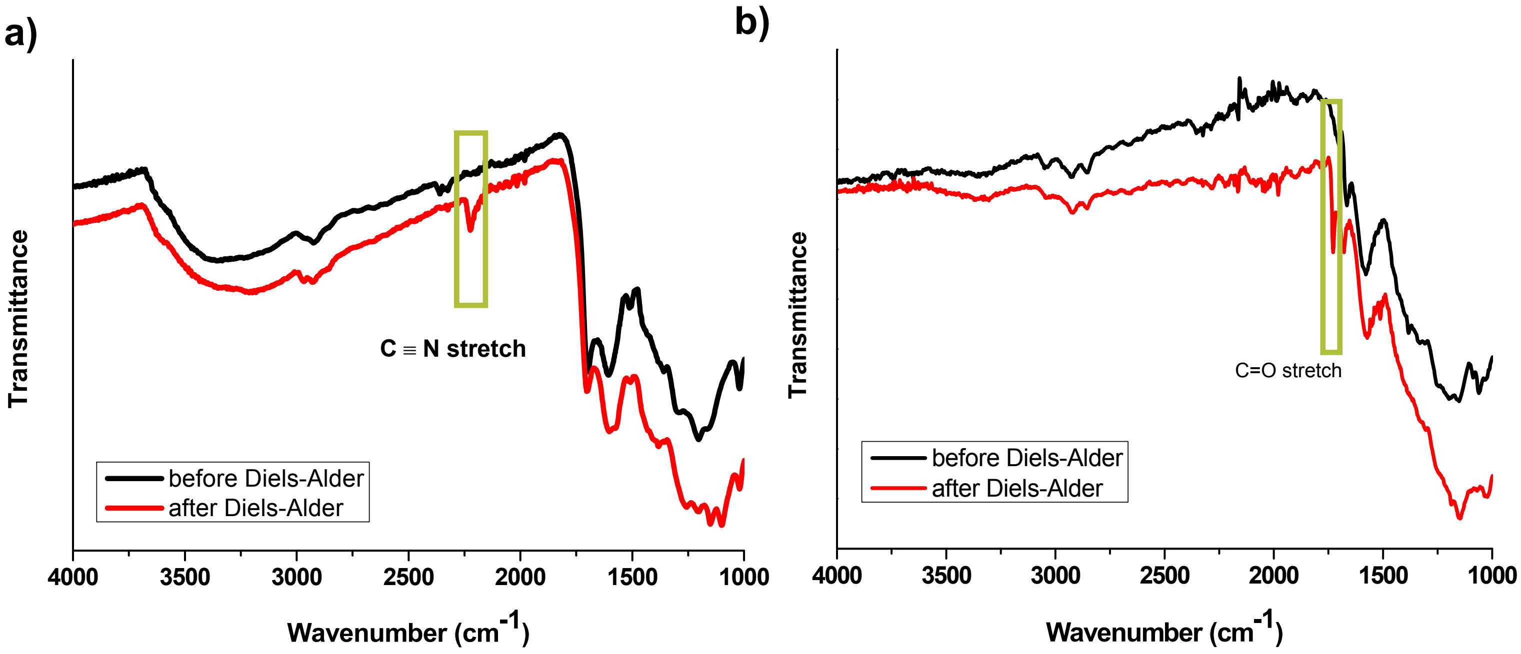


Figure S2. FTIR of DCDTO-functionalized HTC@180 (left) and 550 (right)

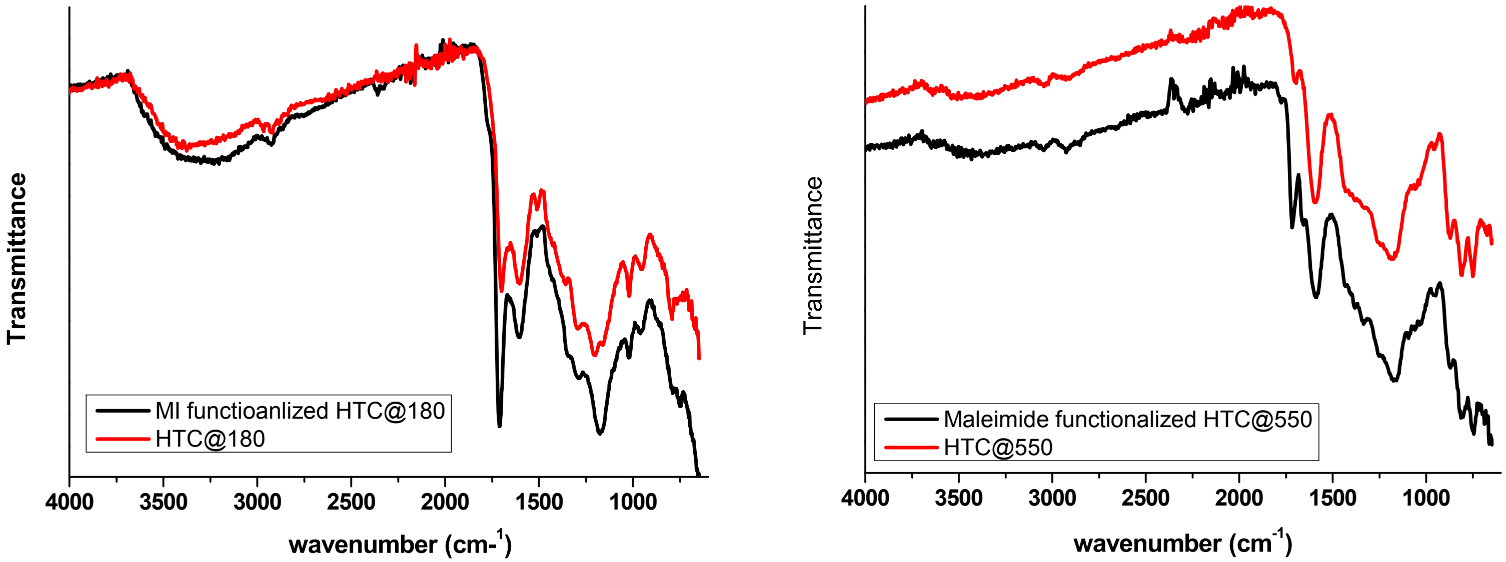


Figure S3. FTIR of maleimide (MI)-functionalized HTC@180 (left) and 550 (right)

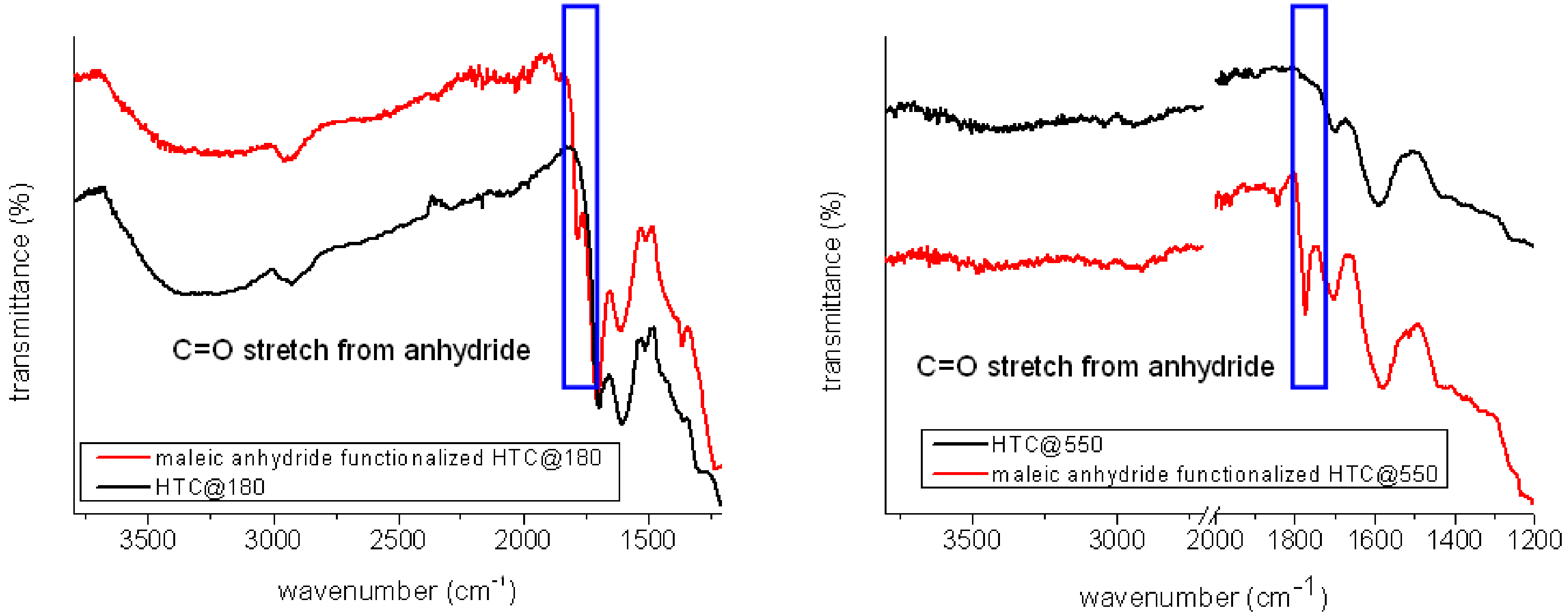


Figure S4. FTIR of maleic anhydride functionalized HTC@180 (left) and 550 (right)

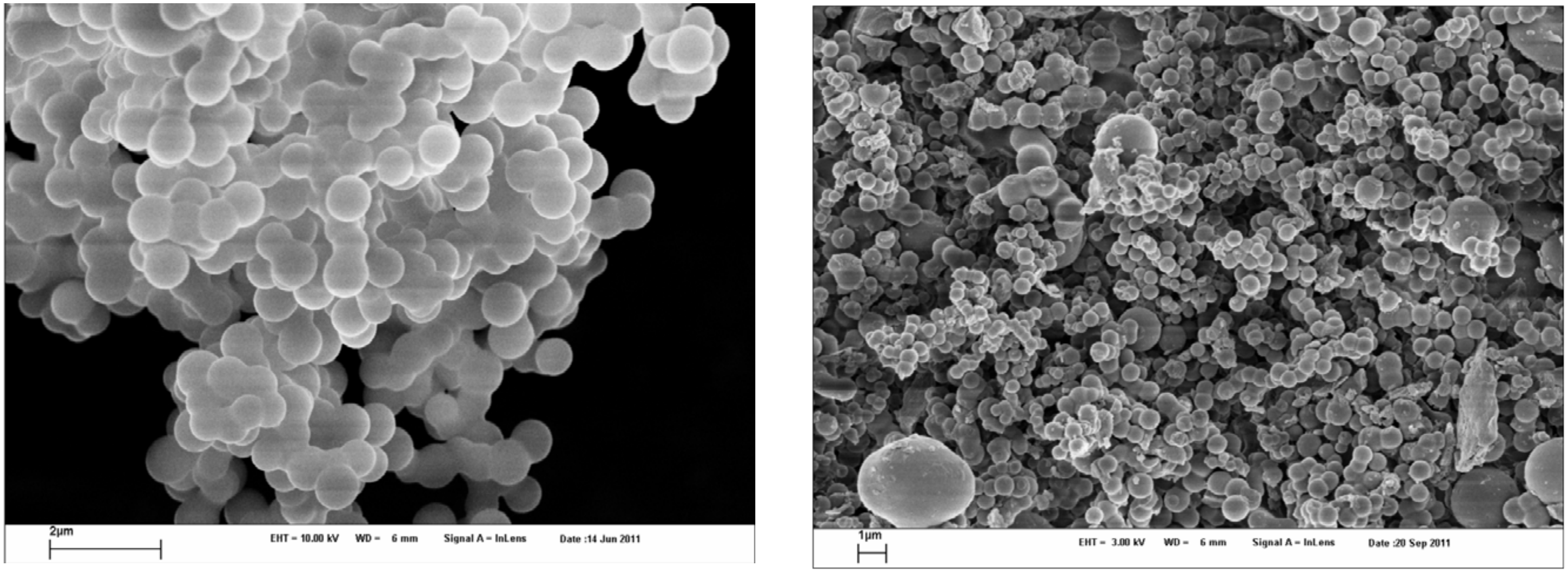


Figure S5. SEM of HTC@180 (left) and thiolated HTC@180 (right). No morphological/size change is observed before and after the acid treatment.

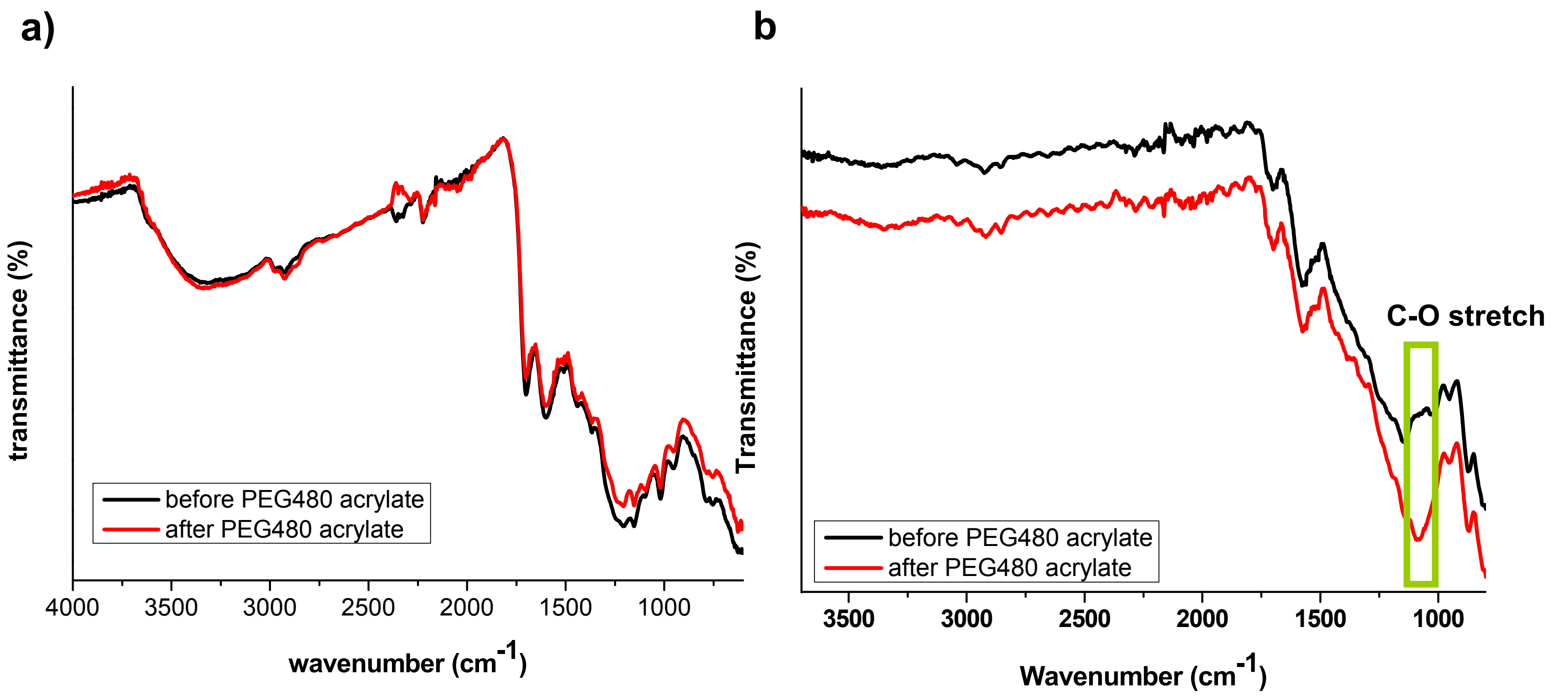
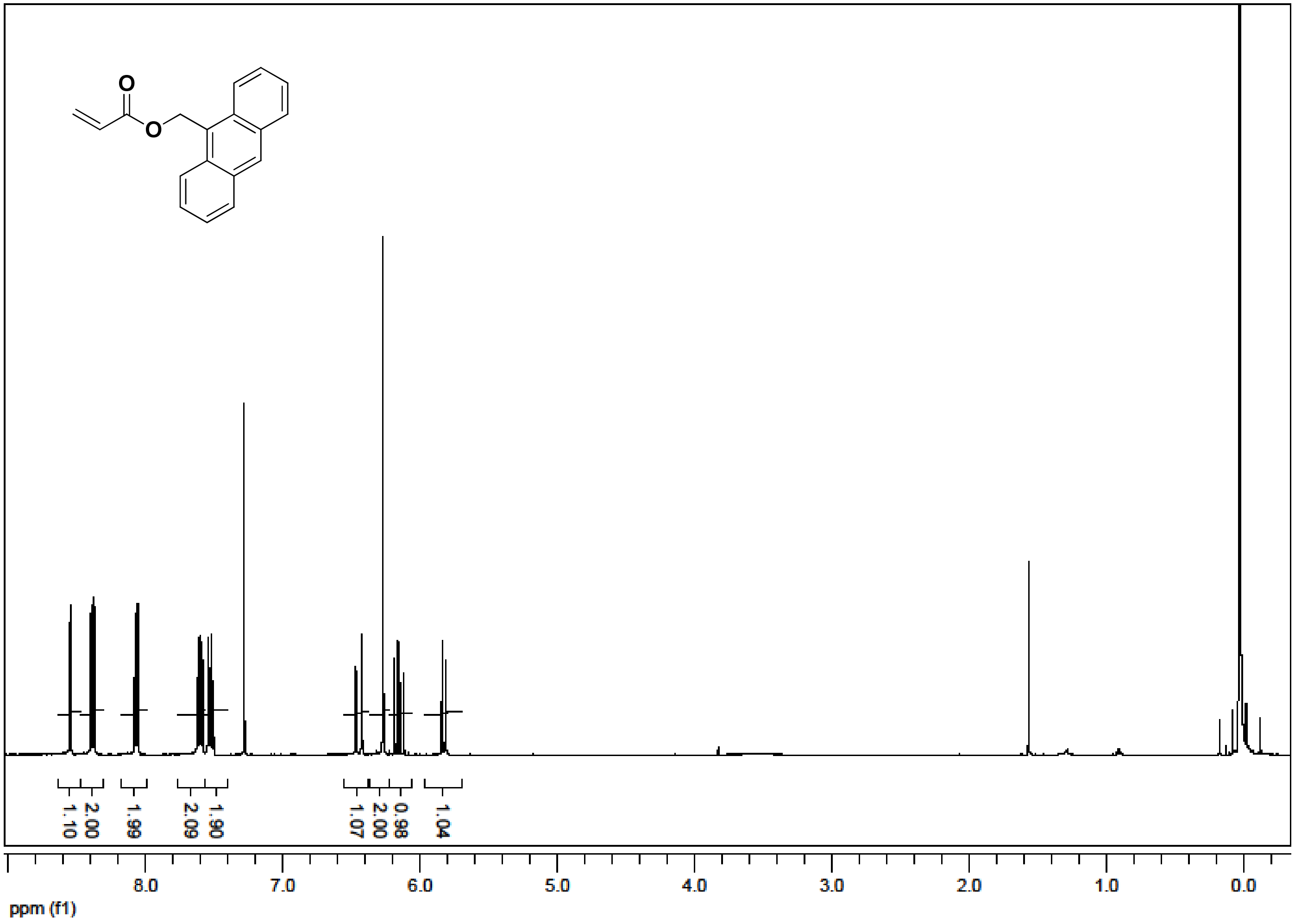
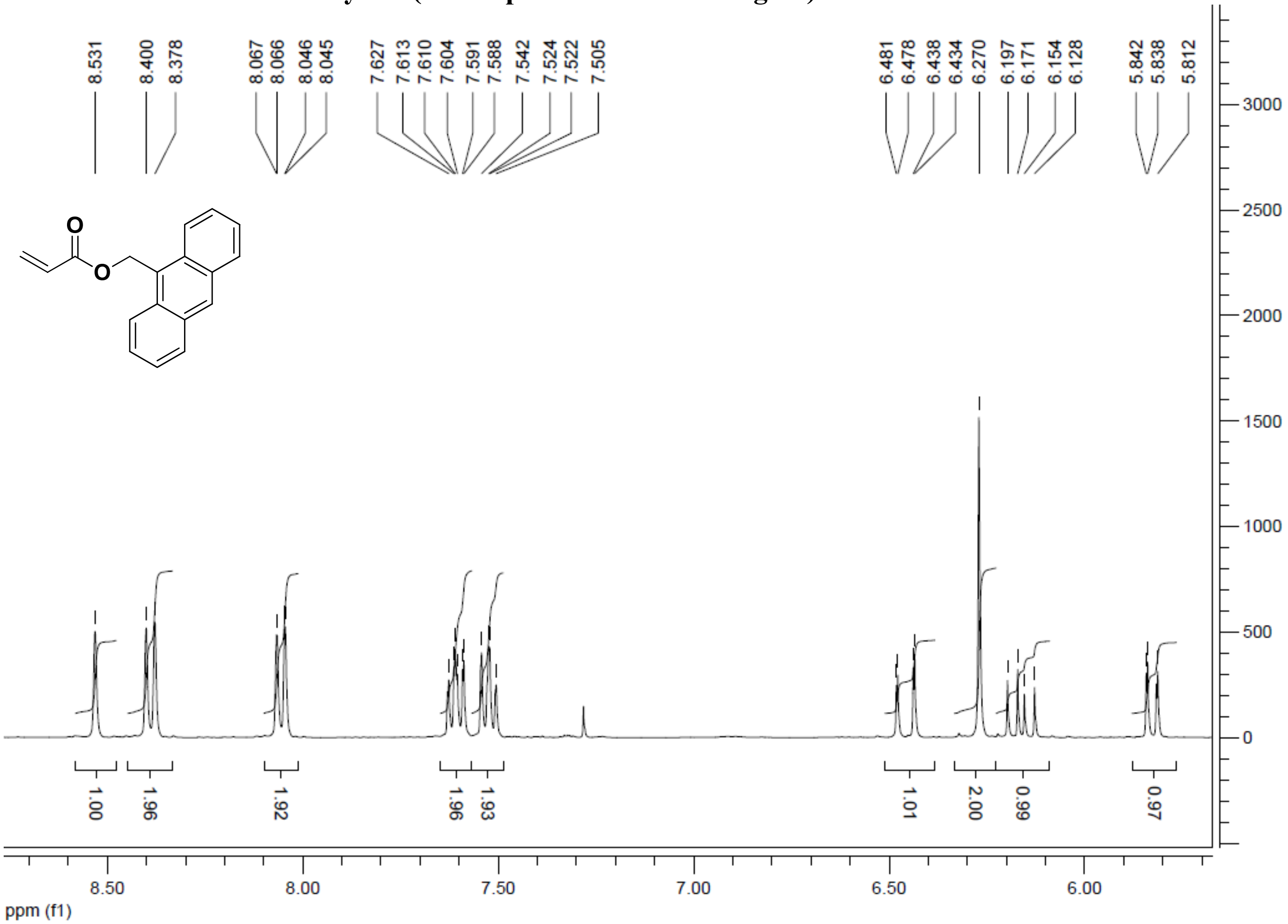


Figure S6. a) After the conjugate addition PEG acrylate onto the DCDTO-HTC@180, b) After the conjugate addition PEG acrylate onto the thiolated-HTC@180.

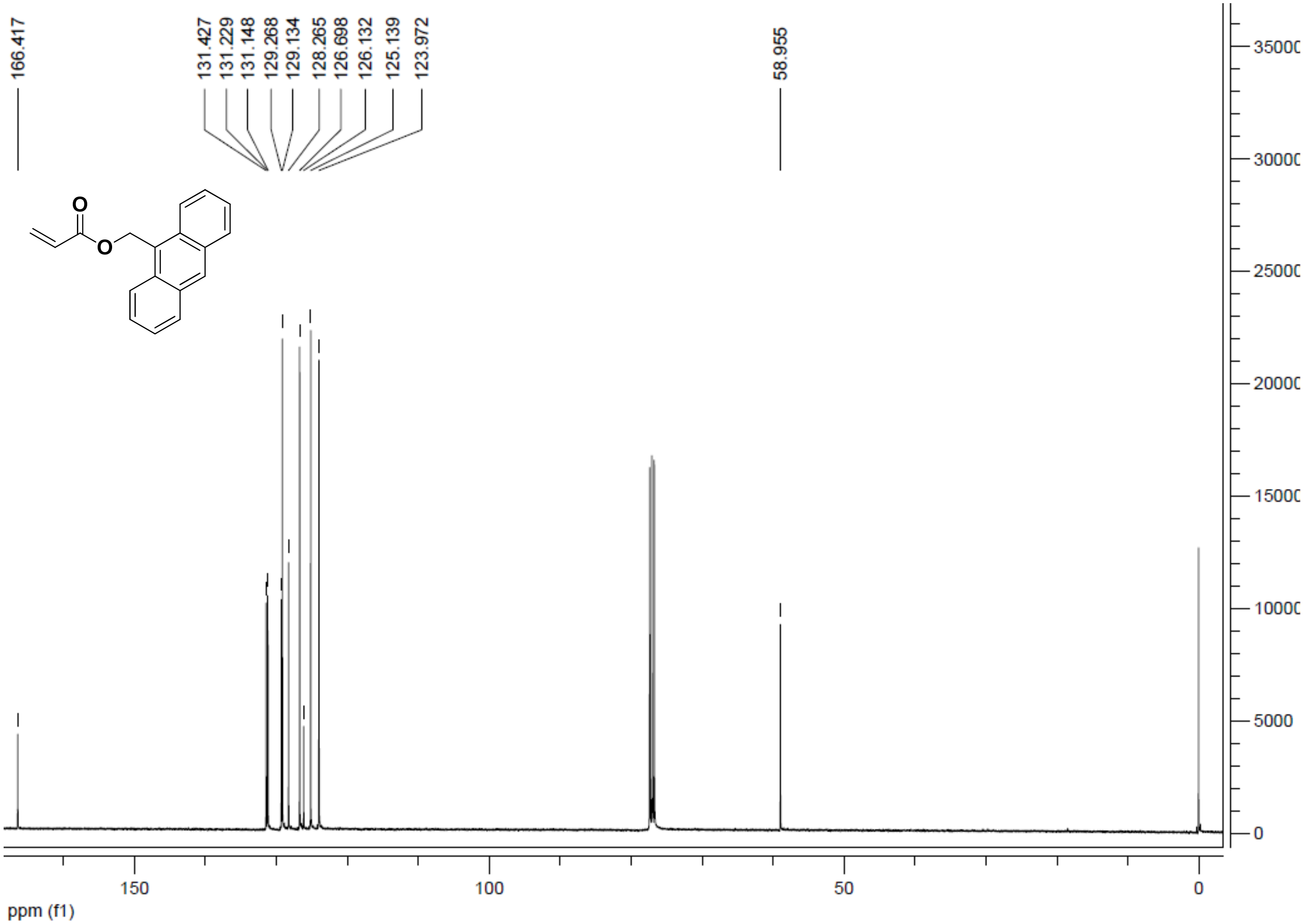
^{1}H-NMR of anthracene acrylate



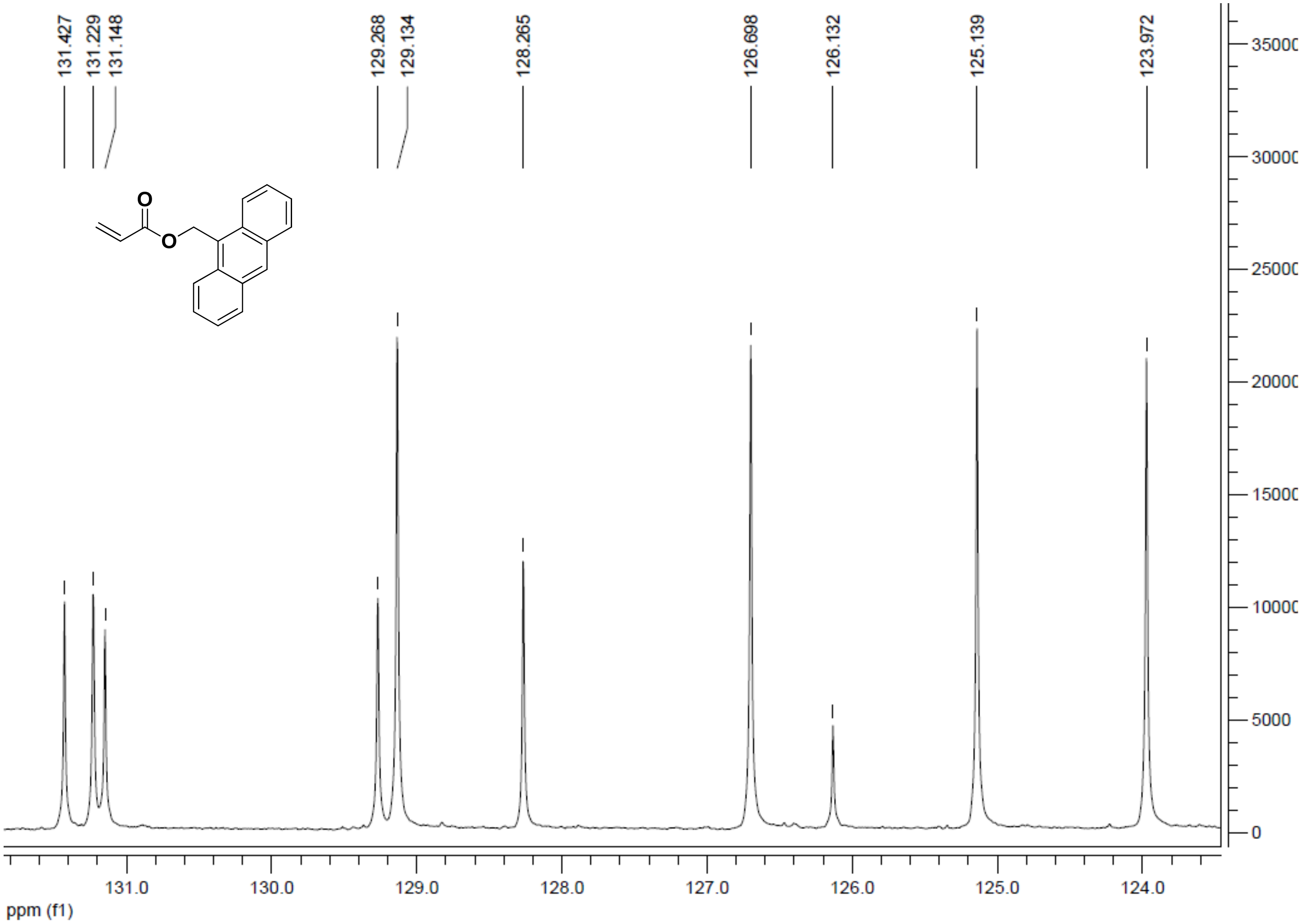
^{1}H-NMR of anthracene acrylate (close up of the aromatic region)



^{13}C-NMR of anthracene acrylate



^{13}C-NMR of anthracene acrylate (close up of the aromatic region)



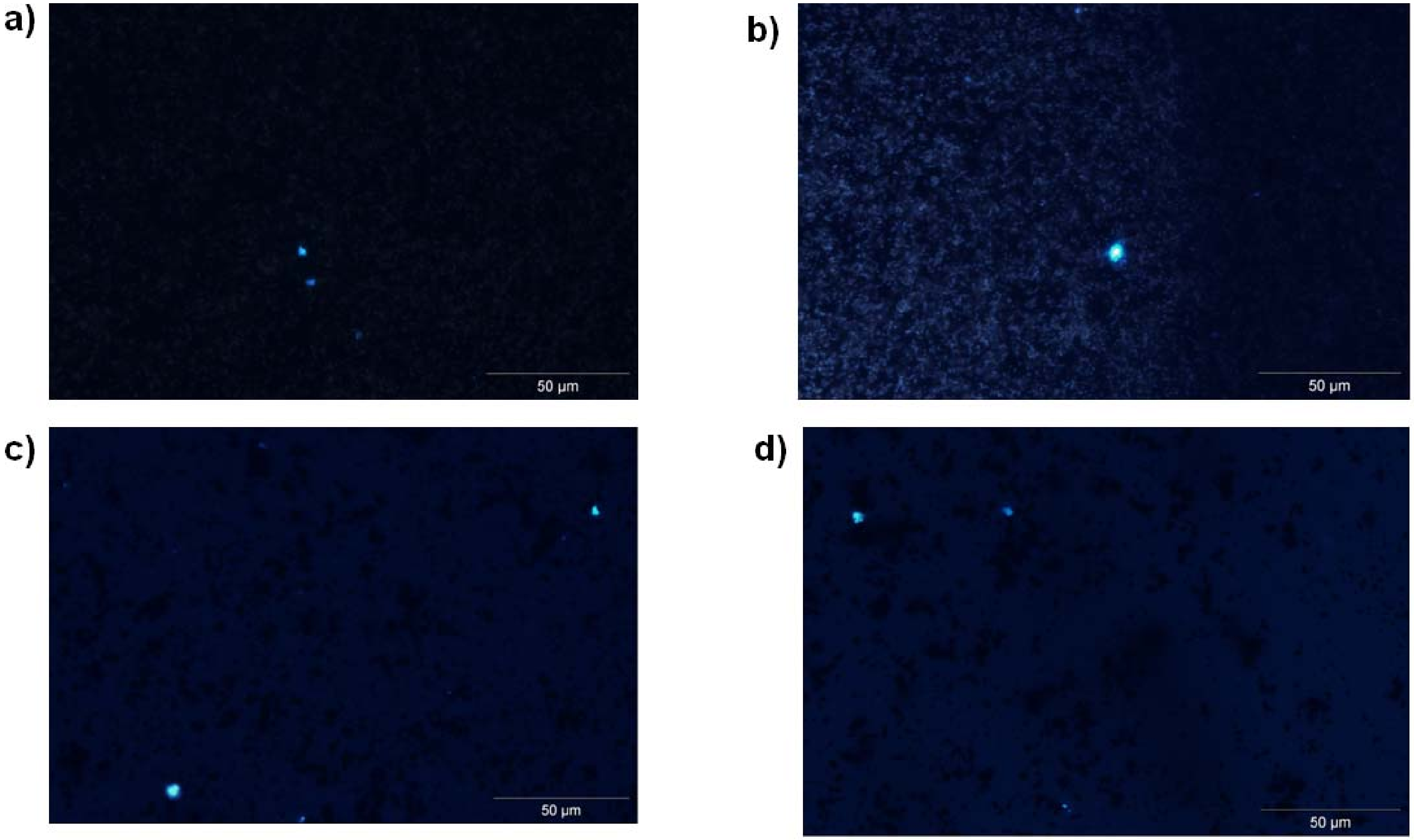


Figure S7. a) HTC@180, b) Fluorescent image of anthracene-functionalized HTC@180, c) HTC@550, d) Fluorescent image of anthracene-functionalized HTC@550. Fluorescent image of anthracene-functionalized HTC@180 only shows fluorescence.