Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supplementary Information:

Adaptive Molecular Quaternary Clips Made by Pyrene Functionalized Polyhedral Oligomeric Silsesquioxane

Tsung-Kai Yang,‡ Jou-Tsen Ou,‡ Heng-Yi Lin, Wei-Cheng Peng, Meng-Hsuan Jao, Jia Chen, Bin Sun,[c] Yu Zhu,[b] and Chien-Lung Wang*[a]

[a]Department of Applied Chemistry, National Chiao Tung University, 1001 University Rd., Hsinchu, Taiwan 30010, E-mail: kclwang@nctu.edu.tw

[b]Department of Polymer Science and Department of Polymer Engineering, University of Akron, Akron, Ohio 44325, United States

[c]State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai, 201620, China

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Experimental Procedures

Materials and Instrumentation

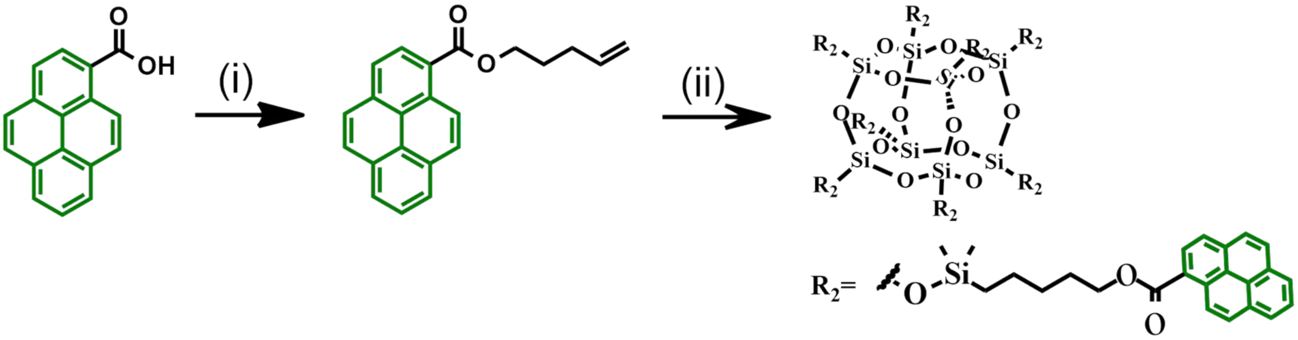
Unless otherwise noted, reagents and solvents were purchased as reagent grade and used without further purification. All reactions were carried out with standard glassware under an inert nitrogen atmosphere. Evaporation and concentration were carried out with water aspirator pressure and drying in vacuum at 10^{-2} Torr. Column chromatography was carried out with SiO_2 60 (230-400 mesh, 0.040-0.063 mm) which was purchased from E. Merck. Thin Layer Chromatography (TLC) was performed on aluminum sheets coated with SiO_2 60 F254 purchased from E. Merck, visualization by UV light. All ^1H NMR spectra which were referenced to the residual proton impurities in the $CDCl_3$ at δ 7.26 ppm were recorded on Agilent 400-MR DD2 at 400 MHz. Field Desorption mass spectroscopy measurements were carried out on the AccuTOF GCX spectrometer (JEOL). All spectra were measured in the positive reflector mode.

Differential Scanning Calorimetry (DSC): DSC results were obtained by a TA Instruments DSC Q20. Nitrogen was used as purge gas as a flow rate of 50.0 ml/min, and samples were scanned from 40°C to 210°C (**Q-clip** and **NDI**). The measurements operated two cycles at a scan rate of 16°C min^{-1}.

X-ray diffractometer (XRD): XRD results were obtained by Bruker APEX DUO single-crystal diffraction. In all cases, a linear monochromatic Cu-K_{α}1 beam (λ = 1.54 Å) was obtained using a rotating I microfocus X-ray generator (18 kW) equipped with an APEX II CCD camera.

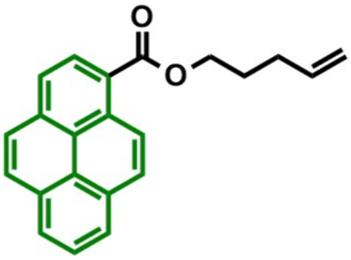
Sample preparation: The mixture samples were prepared by drying the CH_2Cl_2 solutions of the Q-clip:NDI mixtures by rotary evaporator.

General scheme and procedure for preparation of pent-4-en-1yl pyrene-1-carboxylate and Q-Clip:



Scheme S1. Synthetic route of the Q-Clip (i) Pent-4-en-1-ol, DCM, DMAc, DPTS, DIPC, 0℃, 24 h (55%); (ii) polyhedral oligomeric silsesquioxane, diethyl ether, Karstedt's catalyst, rt for 30 min, 40℃ for 24 h (60%).

Synthetic Procedures and Characterization Data



1

Synthesis of pent-4-en-1yl pyene-1-carboxylate (1): 1-pyrenecarboxylic acid (200 mg, 0.81 mmol) was dissolved in dichloromethane (DCM, 30mL) and N,N-dimethylacetamide (DMAc, 2mL), and stirred for 4 h in room temperature. Pent-4-en-1-ol (76.95 mg, 0.89 mmol, 1.1 equiv.), 4-(dimethylamino) pyridinium-4-toluenesulfonate (DPTS, 23.91 mg, 0.24 mmol, 0.3 equiv.), and N,N-diisopropylcarbodiimide (DIPC, 189 µL, 1.22 mmol, 1.5 equiv.) were added into the mixture under ice bath with N_2. After reacting 24h, the reaction mixture was filtered out and washed with a saturated brine solution. The organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed by rotary evaporation. The residue was purified by flash column chromatography, yielding the yellow-green oil-like product, 140 mg (0.46 mmol, 55%).^{1}H NMR (400 MHz, $CDCl_3$) δ 9.27 (d, J = 9.43 Hz, 1H), 8.64 (d, J = 8.11 Hz, 1H), 8.30 – 8.22 (m, 3H), 8.20 – 8.16 (m, 2H), 8.07 (dd, J = 8.11, 14.87 Hz, 2H), 5.92 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.20 – 5.03 (m, 3H), 4.53 (t, J = 6.6 Hz, 2H), 2.34 (q, J = 7.0, 2H), 2.13 – 1.93 (m, 2H).

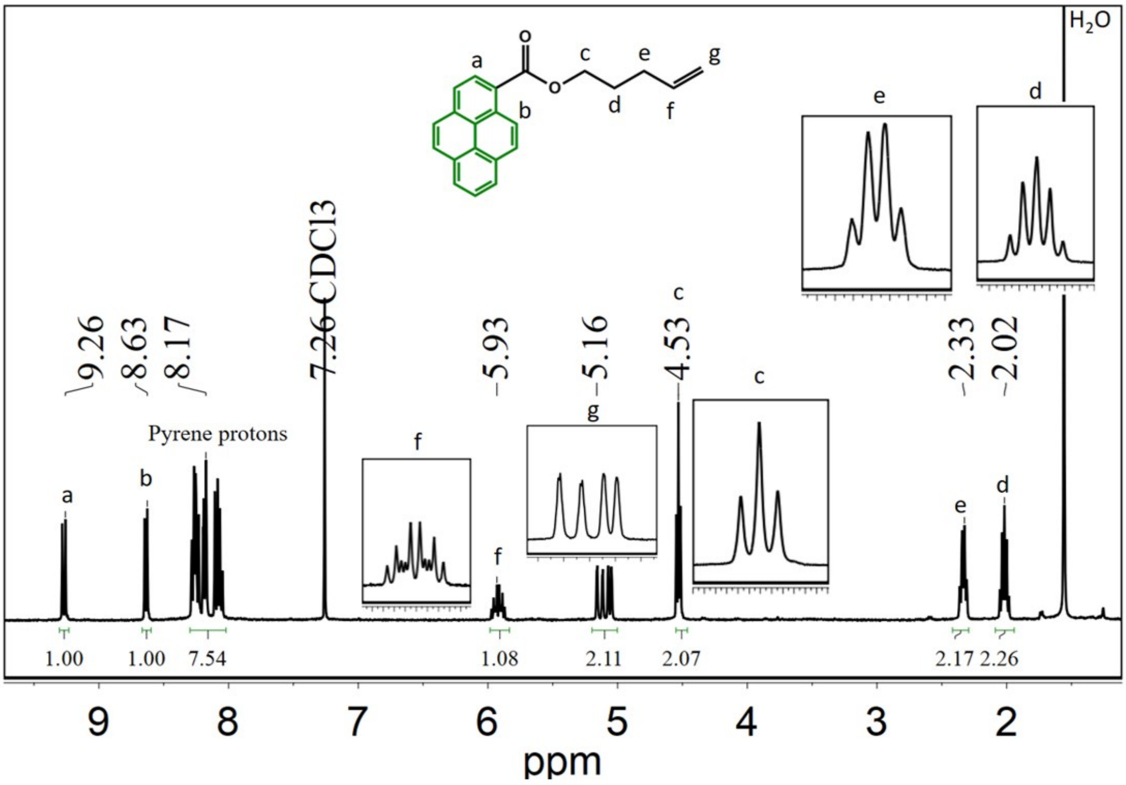


Figure S1 ^{1}H NMR (400 MHz) of pent-4-en-1yl pyrene-1-carboxylate **(1)**.

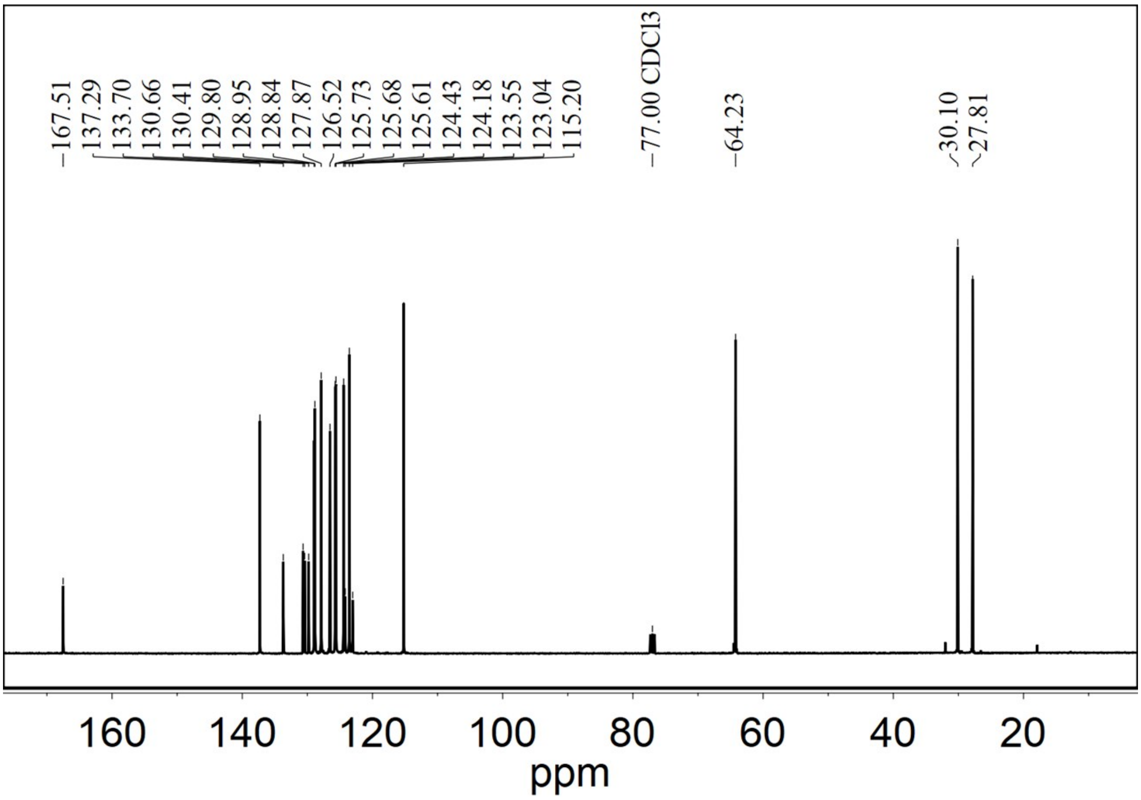


Figure S2 ^{13}C NMR (100 MHz) of pent-4-en-1yl pyene-1-carboxylate **(1)**.

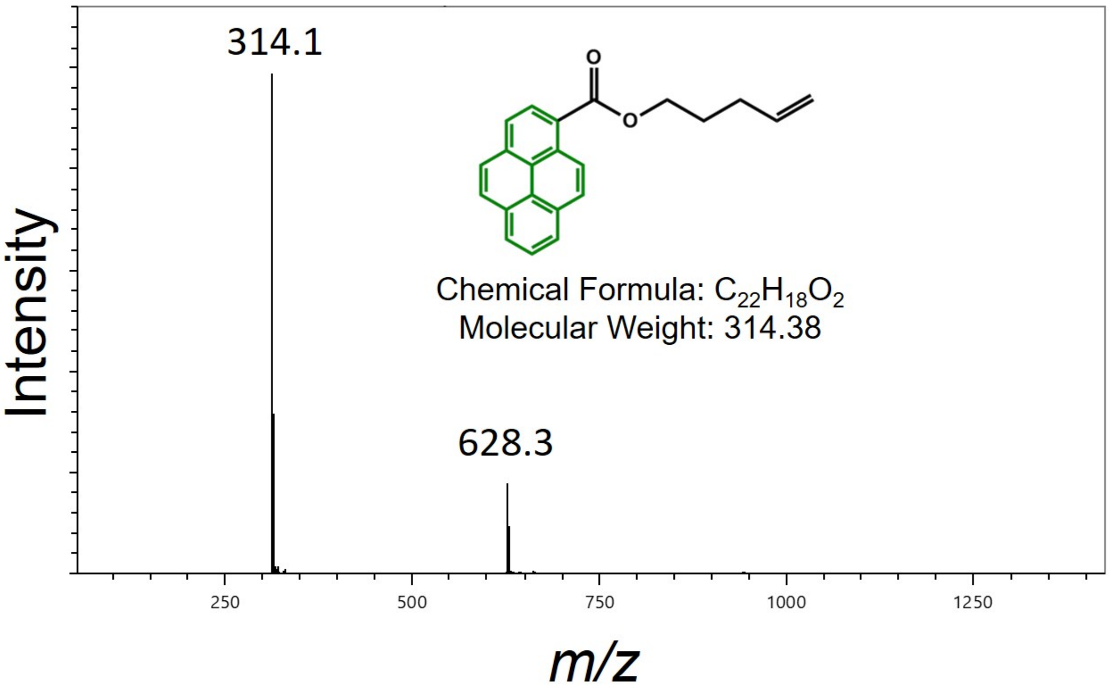
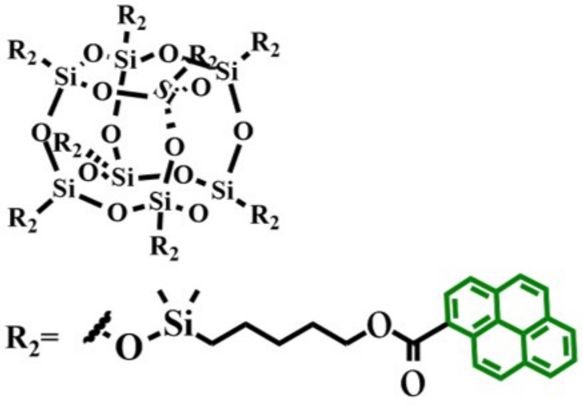


Figure S3 LR-FDMS of pent-4-en-1yl pyrene-1-carboxylate **(1)**.



2

Synthesis of Q-Clip (2): Pent-4-en-1yl pyrene-1-carboxylate (py-ester, 200 mg, 0.64 mmol, 13 equiv.) and platinum (0) -1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (Karstedt's catalyst, 75 μL) were dissolved in 1 mL diethyl ether at room temperature. After stirring for 30 min, polyhedral oligomeric silsesquioxane (POSS, 50 mg, 0.049 mmol, 1 equiv.) was added into the solution and then the reaction mixture was heated to 45℃ for 24 hours with N_2. After cooling to room temperature, the celite was added into the mixture to remove metal catalysts. After removing the solvent, the crude residue was purified by column chromatography through silica gel (toluene/DCM, 1:1 v/v), yielding the green product, 103.9 mg (0.03 mmol, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (d, J = 9.4 Hz, 8H), 8.47 (d, J = 8.1 Hz, 8H), 8.12 – 8.03 (m, 24H), 7.99 - 7.92 (m, 16H), 7.90 (d, J =7.6 Hz, 16H), 7.86 (d, J = 8.9 Hz, 8H), 4.39 (t, J = 6.7 Hz, 16H), 1.87 – 1.73 (m, 16H), 1.52 – 1.39 (m, 16H), 0.67 - 0.61 (m, 16H), 0.15 (s, 48H).

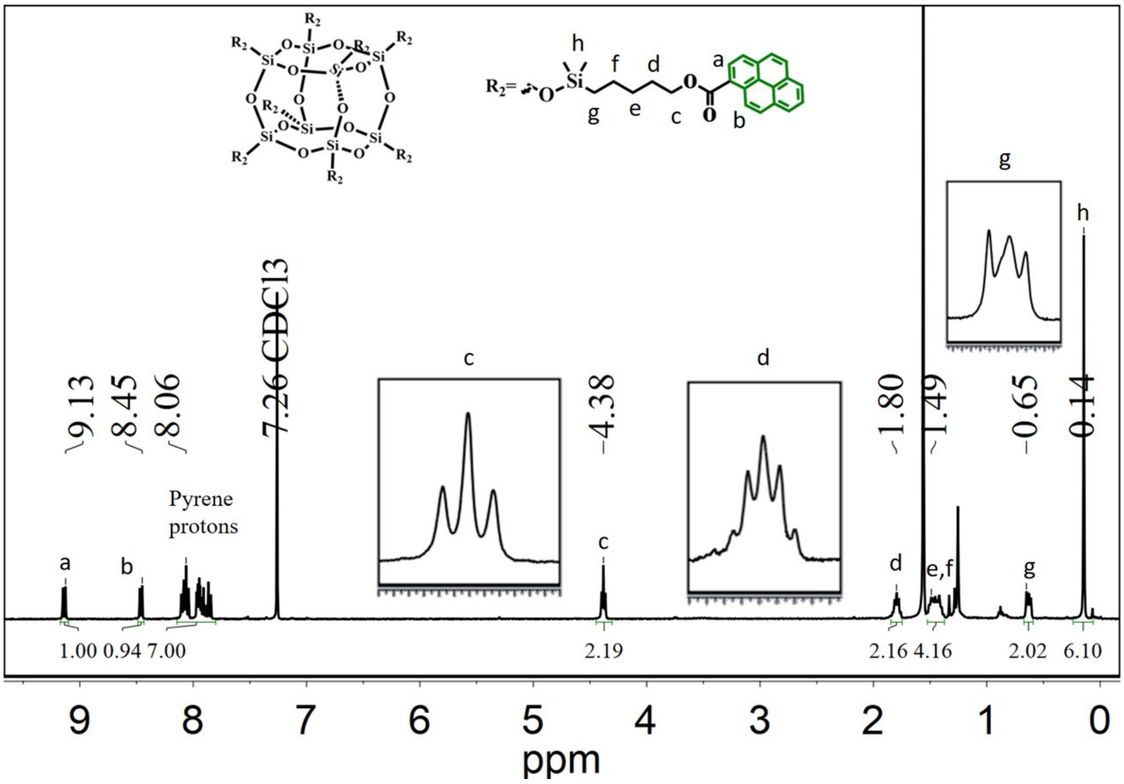


Figure S4 ^{1}H NMR (400 MHz) of **Q-Clip**.

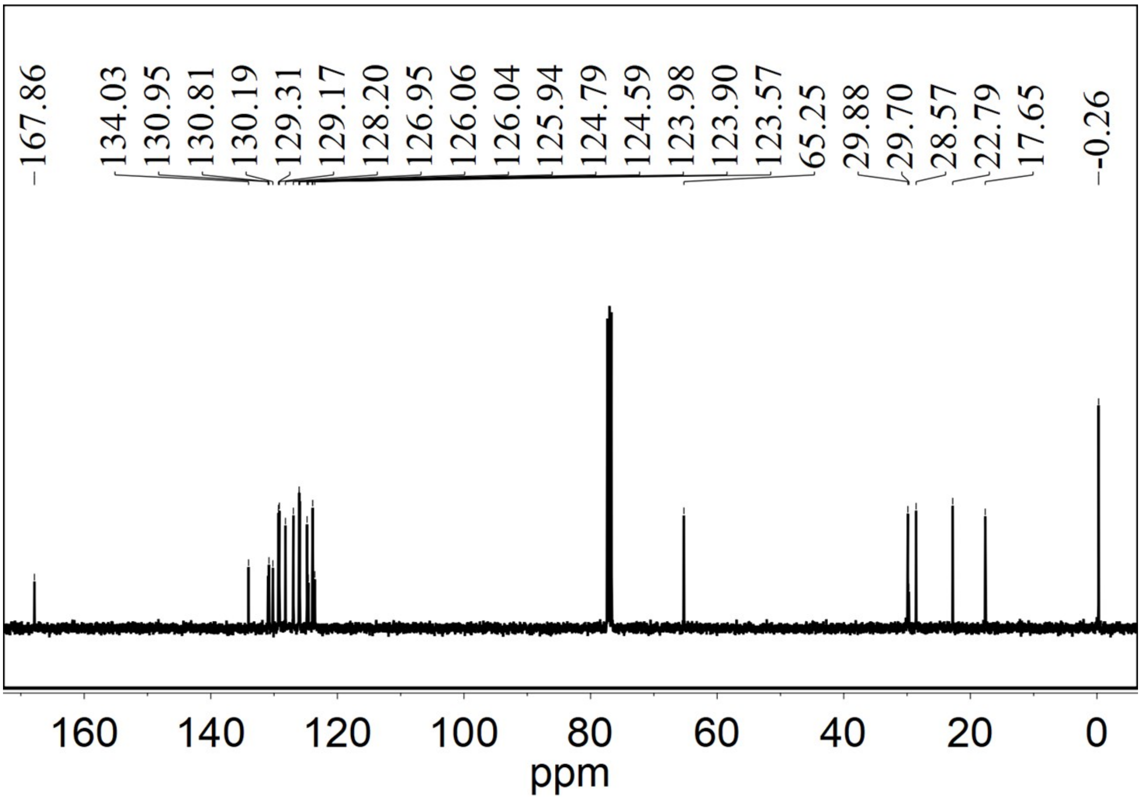


Figure S5 ^{13}C NMR (400 MHz) of **Q-Clip**.

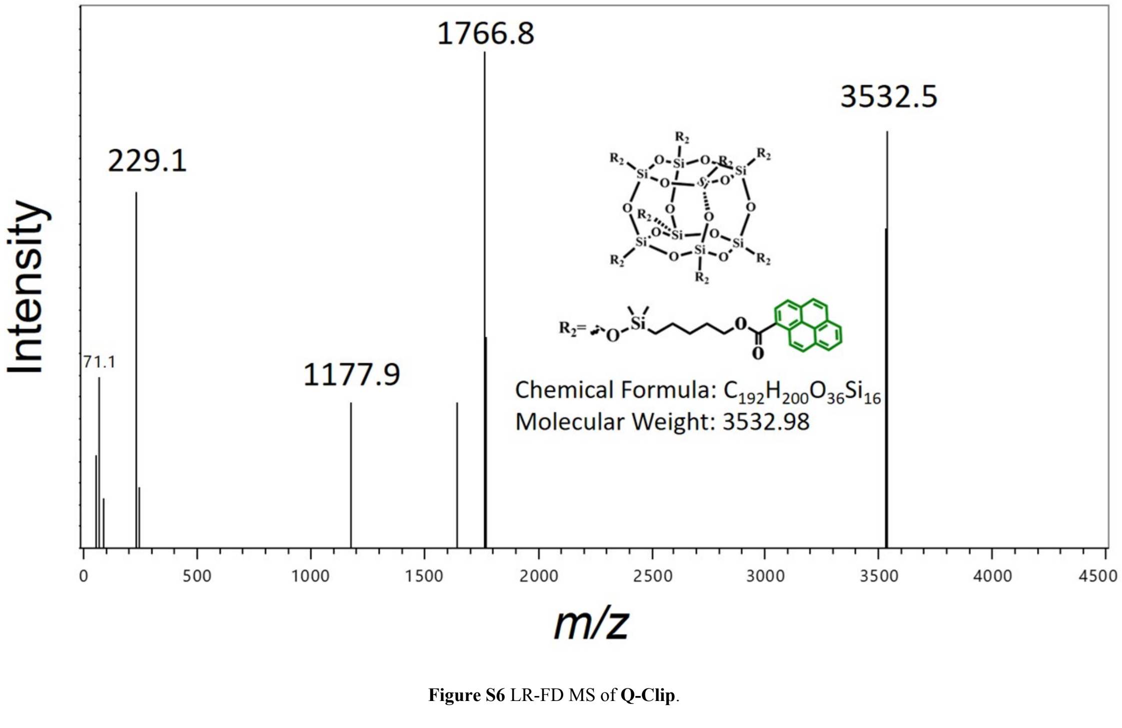
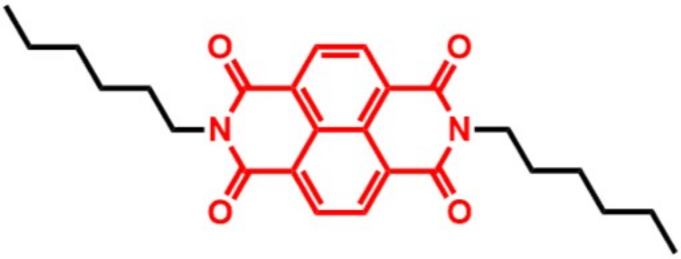


Figure S6 LR-FD MS of **Q-Clip**.



3

Synthesis of NDI (3): 1,4,5,8-Naphthalenetetracarboxylic dianhydride (NDA, 1000.0mg, 3.73mmol, 1equiv.) were dissolved in 75 mL Dimethylformamide (DMF, 75mL). After the reaction mixture became homogeneous, hexylamine (1.08 mL, 8.21 mmol, 2.2 equiv.) was then dropped into the solution. The reaction mixture was heated to 110℃ for 24 h with N_2. The mixture was extracted with DCM and saturated aqueous NaCl solution and the organic layer was then dried over $MgSO_4$. After removing the solvent, the crude residue was purified by column chromatography through silica gel (DCM/hexane, 7:3 v/v), yielding the white needle crystal, 907.6 mg, 56%. ^1H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 4H), 4.20 (t, J = 7.6 Hz, 4H), 1.79 – 1.69 (m, 4H), 1.49 – 1.39 (m, 4H), 1.38 – 1.30 (m, 8H), 0.90 (t, J = 7.0, 6H).

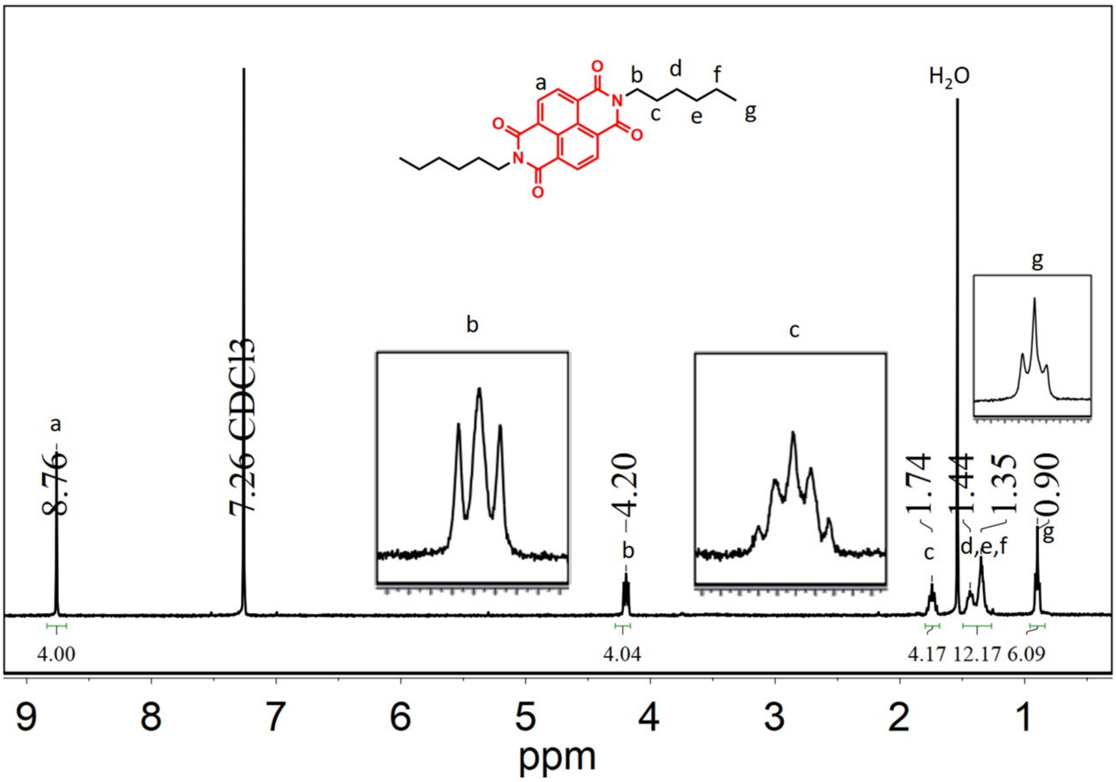


Figure S7 ^1H NMR (400 MHz) of **NDI**.

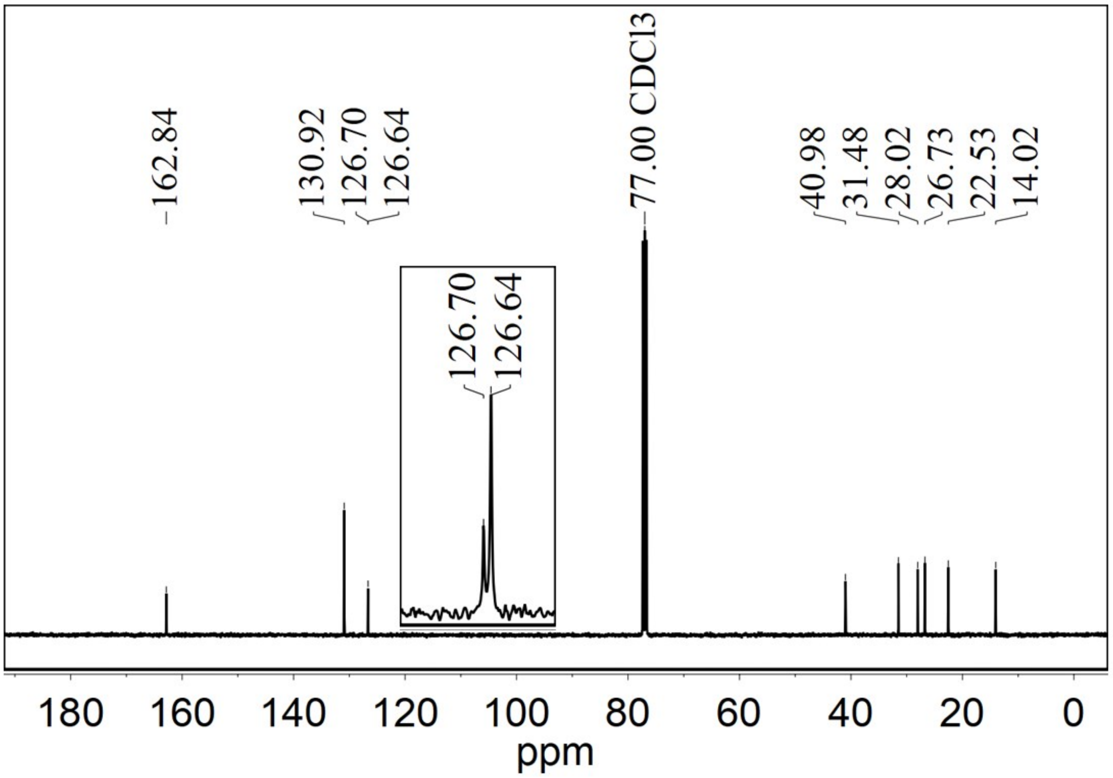


Figure S8 ^{13}C NMR (100 MHz) of **NDI**.

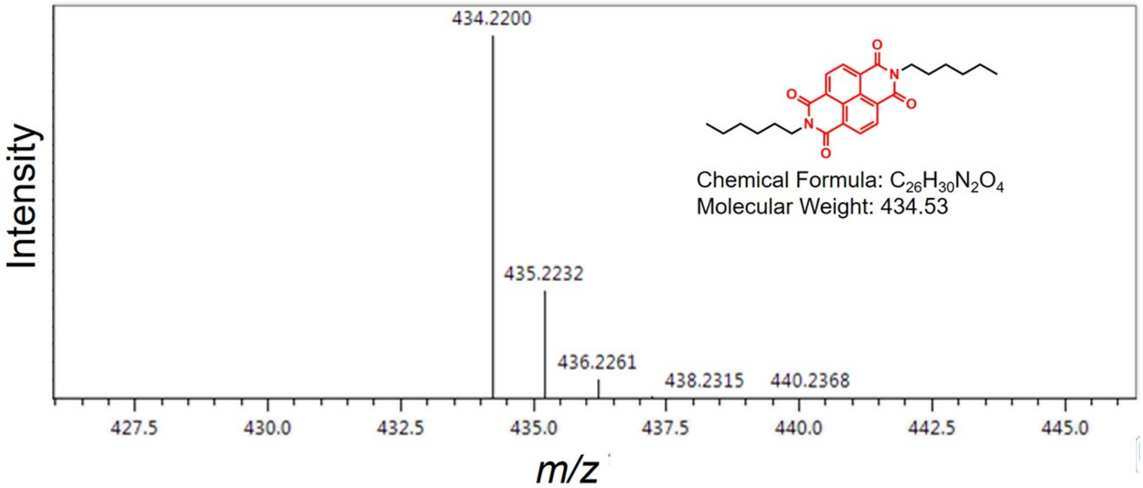


Figure S9 HR-FDMS of **NDI**.

Ultraviolet-Visible experiments

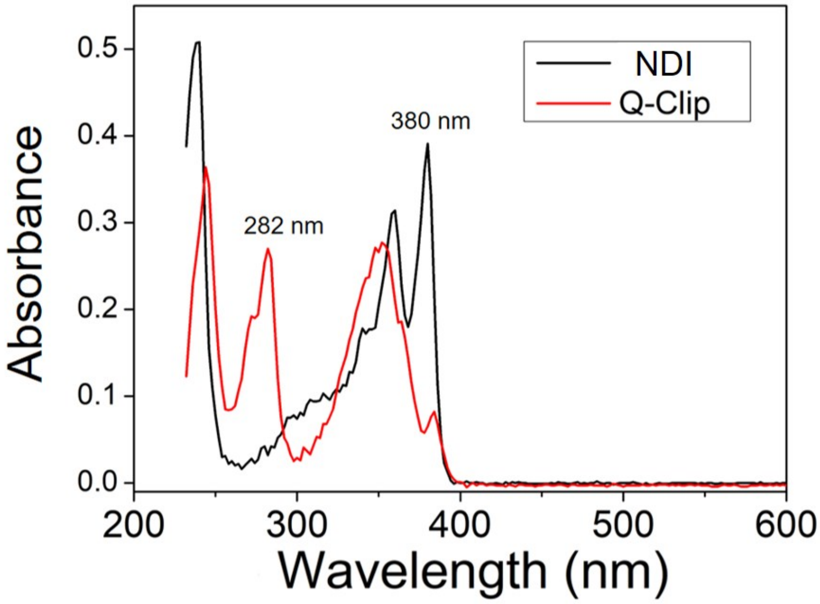


Figure S10 UV/vis spectra of **NDI** and **Q-Clip** (2μM) within CH_2Cl_2 at 298 K.

Fluorescence experiments

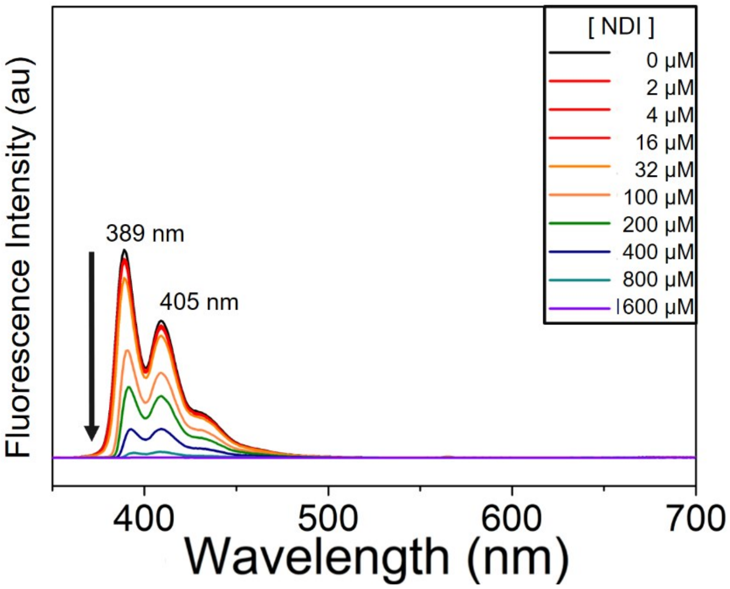


Figure S11 Fluorescence emission spectra (λ_{ex} = 282 nm) of compound **(1)** (16 μM) in the presence of increasing the concentration of **NDI** in CH_2Cl_2 at 298 K.

X-ray structure determination

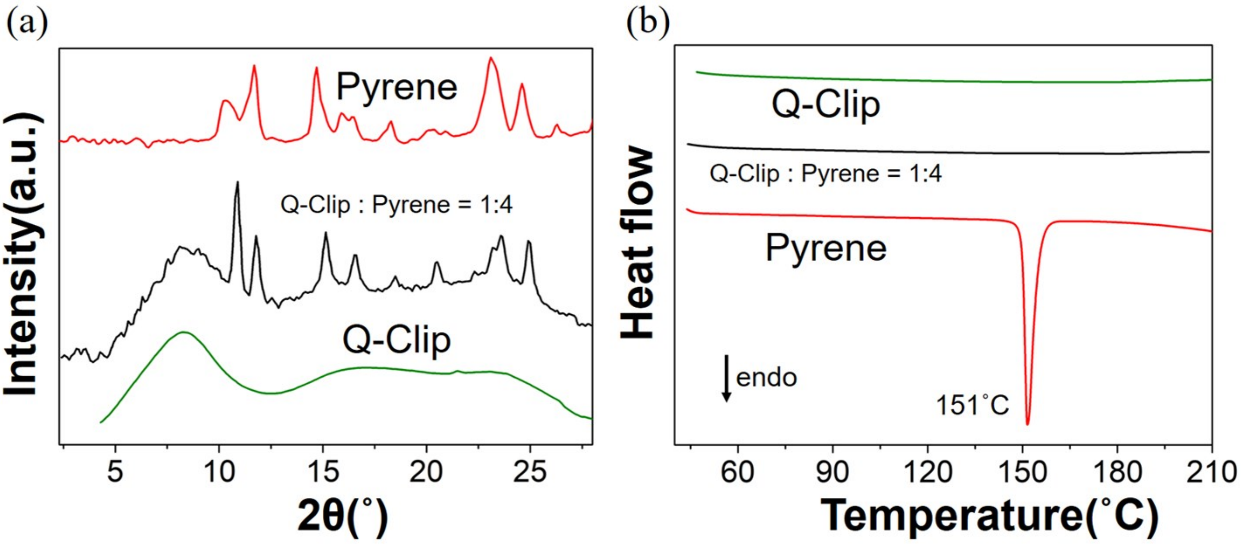


Figure S12. **(a)** The XRD patterns of the **Q-clip**, **pyrene**, and **Q-clip:pyrene** mixtures. (b) The DSC thermograms of **Q-clip**, **pyrene**, and **Q-clip:pyrene** mixtures in the heating course.