Electronic Supplementary Information for

Efficient Green-Red Piezofluorochromism of Bisanthracene-Modified Dibenzofulvene†

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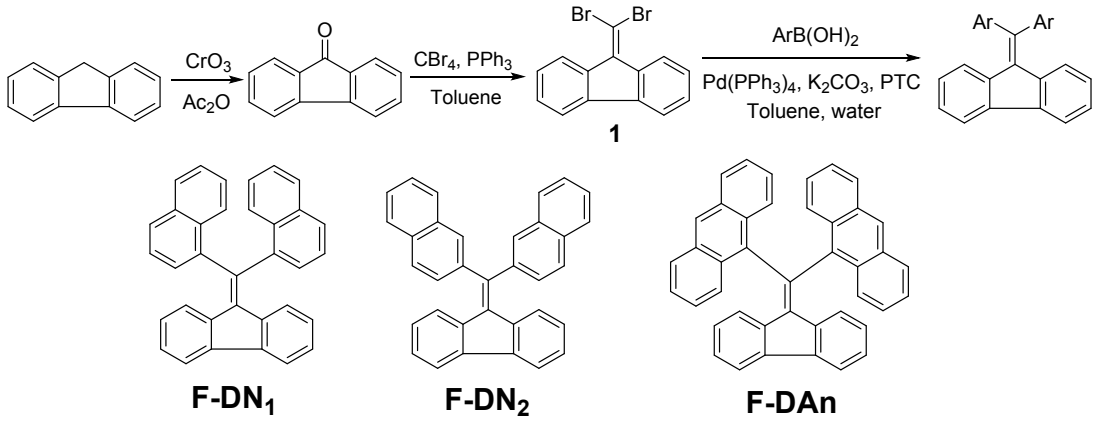
1. Experimental details

All commercially available starting materials, reagents and solvents were used as supplied, unless otherwise stated, and were purchased from Aladdin, Energy, and Sinopharm Chemical Reagent Co. Ltd. All reactions were carried out under a dry nitrogen atmosphere and the temperatures were measured externally. THF and toluene were dried using sodium wire and benzophenone as the indicator. Reported yields are isolated yields. Purification of all final products was accomplished by gravity column chromatography, using silica gel. For qualitative purity tests of all intermediates and final products, a single spot (visualised using UV-light at 254 nm and 365 nm) was obtained. ^{1}H NMR (400 MHz or 600 MHz) and ^{13}C NMR (100 MHz or 150 MHz) in $CDCl_3$ were measured on a Bruker AV400 or AV600 spectrometer, and reported in parts per million (PPM) relative to tetramethylsilane as an internal standard. Fourier transform infrared and Raman spectrometer was record on vertex 70 (Bruker). UV-Vis and photoluminescence spectra were recorded on shimadzu UV-VIS-NIR spectrophotometer (UV-3600) and Edinburgh instruments (FLSP920 spectrometers), respectively. λ_{max} (abs) is the lowest energy absorption peak at concentration = 1 x 10^{-5} M, λ_{em} was measured using their respective λ_{max} (abs) as excitation wavelength, for λ_{em}, concentration = 1 x 10^{-5} M. The Mass Spectrometry was recorded on matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF) using Cyano-4-hydroxycinnamic Acid (CHCA) as the matrix or Agilent (1100 LC/MSD Trap). The energy levels of three compounds were obtained from the simulation based on Gaussian program. Fluorescence imaging microscope (CLSM) were operated and carried out on the commercial LSM 710 system (Carl Zeiss Company, Germany). For X-ray Crystallographic Studies, diffraction data were collected at room temperature or low temperature using a Apex Duo X-ray CCD diffractometer working with graphite-monochromatized Moκα X-radiation (λ = 0.71073 Å). Data collection, frame integration, data reduction using multi-scan method, and structure determination were carried out using APEX2 attached software. Empirical absorption corrections were applied to the data using the SADABS program. Structural refinements were performed by the full-matrix least-squares method on F^2 with SHELXTL-97 program. Anisotropic displacement parameters were refined for all nonhydrogen atoms. Hydrogens bonds to carbon atoms were placed at calculated positions with the appropriate AFIX instructions and refined using a riding model. Related parameters of some short contacts (such as π···π and C-H···π) in the crystal structures are measured using PLATON,[1] Mercury and Diamond softwares. Dihedral angles between the neighbouring planes are calculated using Mercury software with all the atoms on one same aryl ring selected as a plane. With respect to X-ray powder diffraction, powder XRD patterns were obtained using a X'Pert PRO diffractometer from 2θ = 5° to 80° with Cu-Kα radiation (λ = 1.5406 Å) under room temperature.

1. Synthesis:



Scheme S1. Synthesis route to dibenzofulvene derivatives.

Synthesis of 9-(dibromomethylene)-9H-fluorene (1): 16.6 g of fluorene (0.1 mol) was added into a 500 ml round bottom flask with 300 ml acetic anhydride, and the reaction mixture was cooled with iced bath and stirred for 30 min. Then, 25 g of Chromium trioxide (0.25 mol) was poured into the reaction mixture at 0°C with three times in two hours. After the solution was stirred overnight, the resultant mixture was poured into ice water, neutralized with NaOH aqueous solution (1 M), extracted with dichloromethane for three times. The organic layer was combined and dried with Na_2SO_4 for several hours. After filtration, the residue was obtained using rotary evaporator to remove the solvent. The product was purified by column chromatography using DCM/PE (2:8, v/v) as the eluent, and afforded as bright yellow solid (15.5g, 85% yield). After dried in the oven, 9-fluorenone was used directly in the next step.

9-(dibromomethylene)-9H-fluorene was synthesized following the reported procedures with little modifications.[2] Typically, A mixture of 9-fluorenone (9.1 g, 50 mmol), carbon tetrabromide (33.16 g, 100 mmol), and triphenyl phosphine (52.45 g, 200 mmol) in 300 ml of dichloromethane (DCM) was run at 40°C for 24 hours. On cooling to room temperature, the excess solvent was removed by rotary evaporator. After the residue was purified by column chromatography on silica gel using hexane as the eluent, the product was recrystallized in ethanol to afford 11.93 g of 9-(dibromomethylene)-9H-fluorene as a light yellow needle-like crystalline solid (71% yield). ^{1}HNMR ($CDCl_3$, 400 MHz) δ (ppm): 8.584 (d, J = 8.0 Hz, 2H), 7.650 (d, J = 7.6 Hz, 2H), 7.383 (t, J = 7.6 Hz, 2H), 7.277 (t, J = 7.6 Hz, 2H). ^{13}CNMR ($CDCl_3$, 100 MHz) δ (ppm): 140.437, 139.387, 138.049, 129.384, 127.321, 125.953, 119.532.

*9-(di(naphthalen-1-yl)methylene)-9H-fluorene (**F-DN$_1$**)*: To a two-neck flask (100 ml), 1,1-dibromo-2,2-diphenylene (1) (1.01 g, 3 mmol), naphthalen-1-yl-1-boronic acid (1.58 g, 9 mmol), $Pd(PPh_3)_4$ (347 mg, 0.3 mmol), tetrabutyl-ammonium hydrogen sulfate (102 mg, 0.3 mmol), K_2CO_3 (1.25 g, 9 mmol) in toluene (40 ml) and water (20 ml) were added and heated to 90°C and stirred under nitrogen overnight. After cooling down to room temperature, the organic layer was separated and the water layer was extracted with DCM. The combined organic solution was dried with Na_2SO_4 for several hours. After filtration, the resulting solution was concentrated by rotary evaporator. The residue was purified by column chromatography on silica gel using DCM/PE (v/v: 1:9) as the eluent to afford 9-(di(naphthalen-1-yl)methylene)- 9H-fluorene (**F-DN$_1$**) (1.02 g, 79 %)

as light yellow solid. ^{1}HNMR ($CDCl_3$, 600 MHz) δ (ppm): 8.346 (d, J = 8.4 Hz, 2H), 7.899 (d, J = 7.8 Hz, 2H), 7.851(d, J = 8.4 Hz, 2H), 7.654 (d, J = 7.2 Hz, 2H), 7.522 (d, J = 7.2 Hz, 2H), 7.474 (t, J = 8.2 Hz, 2H), 7.398 (m, 4H), 7.150 (t, J = 7.2 Hz, 2H), 6.686 (t, J = 7.8 Hz, 2H), 6.104 (d, J = 7.8 Hz, 2H). ^{13}CNMR ($CDCl_3$, 150 MHz) δ (ppm): 141.110, 140.709, 137.652, 137.559, 137.421, 134.076, 130.779, 128.426, 128.032, 127.894, 126.879, 126.851, 126.136, 126.039, 125.831, 125.281, 124.910, 119.145. MALDI-TOF MS: found: 430.438.

*9-(di(naphthalen-2-yl)methylene)-9H-fluorene (**F-DN$_2$**):* The synthetic procedure for the preparation of **F-DN$_2$** (as light yellow solid) is similar to **F-DN$_1$**. Yield 82%. ^{1}HNMR ($CDCl_3$, 400 MHz) δ (ppm): 7.866 (m, 6H), (d, J = 7.8 Hz, 2H), 7.774 (d, J = = 7.2 Hz, 2H), 7.713 (d, J = 7.6 Hz, 2H), 7.475 (m, 6H), 7.216 (overlapped with solvent, t, J = 7.2 Hz, 2H), 6.829 (t, J = 7.6 Hz, 2H), 6.701 (m, 2H). ^{13}CNMR ($CDCl_3$, 100 MHz) δ (ppm): 145.201, 140.560, 140.442, 138.825, 133.479, 133.137, 129.586, 128.496, 128.406, 128.292, 128.179, 127.816, 127.734, 126.590, 126.512, 126.340, 124.964, 119.303. MALDI-TOF MS: found: 430.454.

*9,9'-((9H-fluoren-9-ylidene)methylene)dianthracene (**F-DAn**)*: The synthetic procedure for the preparation of **F-DAn** (yellow powder) is also similar to **F-DN$_1$**. Yield 72%. FTIR: 3080.18, 3047.76, 2923.07, 1937.00, 1621.86, 1545.08, 1516.02, 1474.74, 1443.47, 385.16, 1348.29, 1303.27, 1281.88, 1254.70, 1225.46, 1162.80, 1138.35, 1111.29, 1019.56, 974.79, 955.83, 935.49, 921.56,891.80, 880.58, 874.56, 837.97, 783.86, 777.65, 724.48, 691.74, 660.96, 639.08, 620.26, 602.67, 588.01, 537.75, 492.95, 424.73, 412.11. ^{1}HNMR ($CDCl_3$, 400 MHz) δ (ppm): 8.507 (s, 2H), 8.399 (d, J = 8.8 Hz, 4H), 7.969 (d, J = 8.4 Hz, 4H), 7.648 (d, J = 7.6 Hz, 2H), 7.300 (t, J = 7.6 Hz, 4H), 7.077 (m, 6H), 6.515 (t, J = 7.6 Hz, 2H), 5.922 (d, J = 8.0 Hz, 2H). ^{13}CNMR ($CDCl_3$, 100 MHz) δ (ppm): 144.871, 140.945, 138.074, 137.121, 136.411, 131.818, 131.592, 129.322, 129.042, 128.066, 126.862, 126.722, 126.312, 125.337, 125.025, 119.145. MALDI-TOF MS: found: 530.531. Melting point: >280 ^{o}C.

2. NMR spectra.

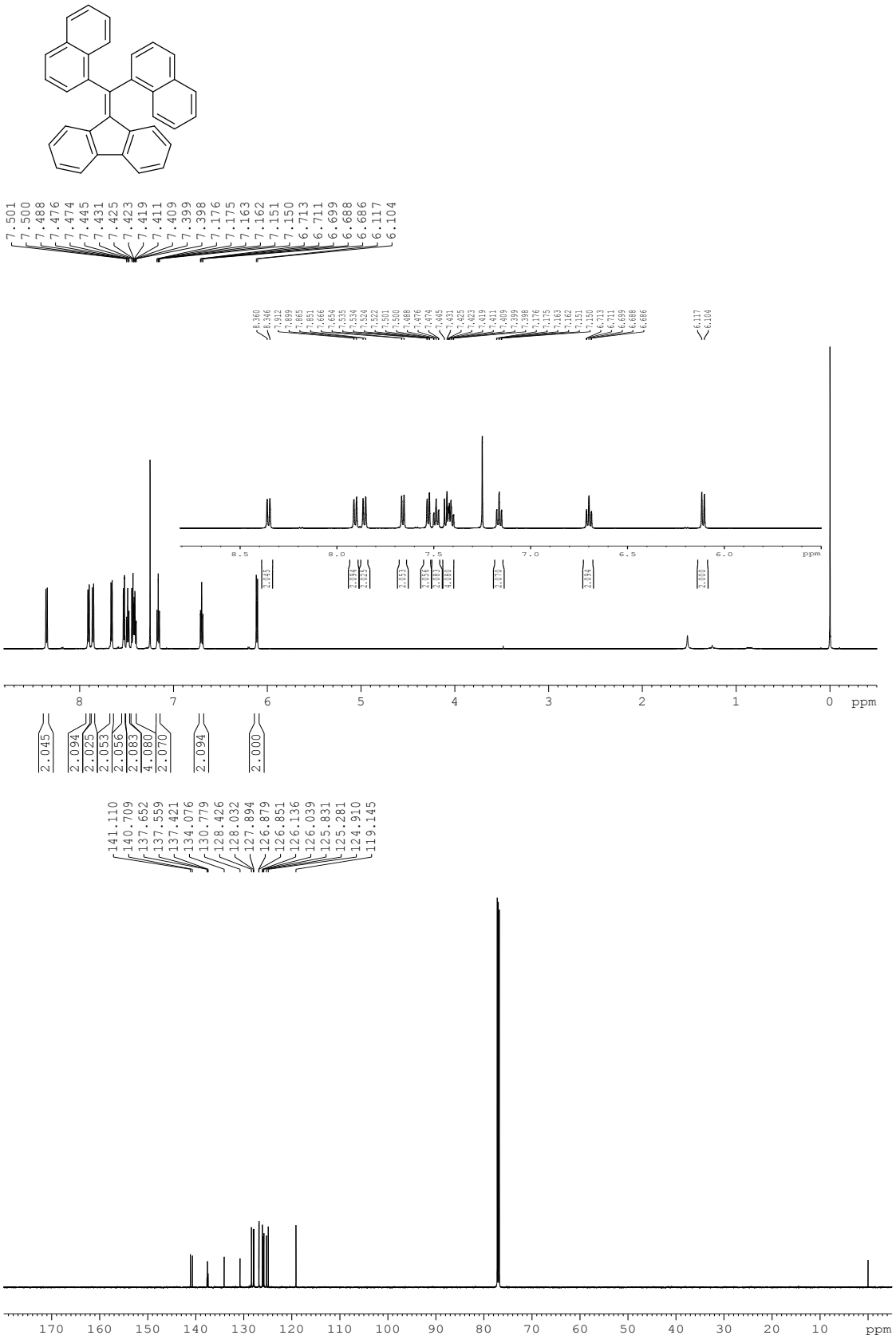


Figure S1 NMR spectra of F-DN_1.

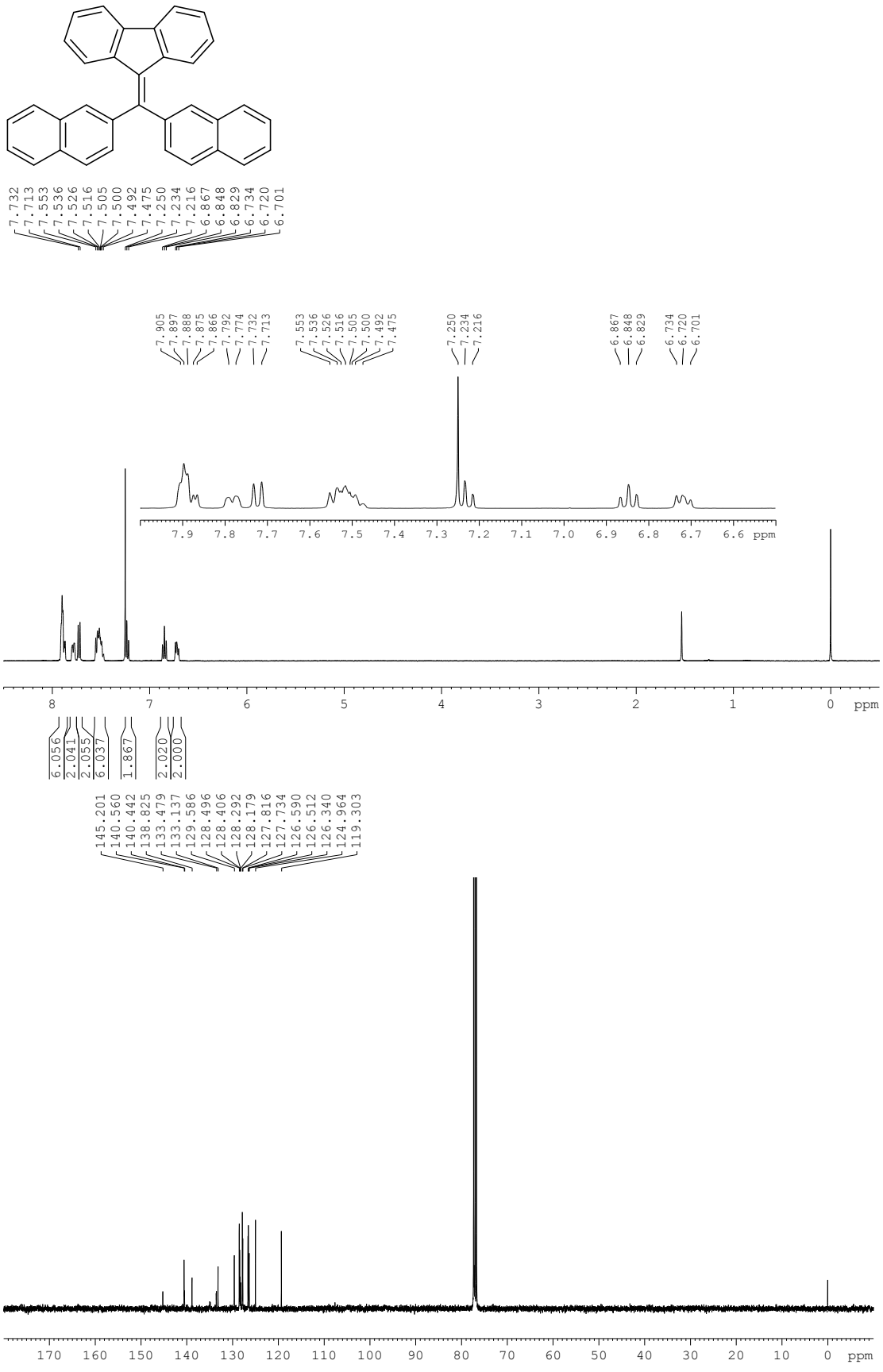


Figure S2 NMR spectra of F-DN_2.

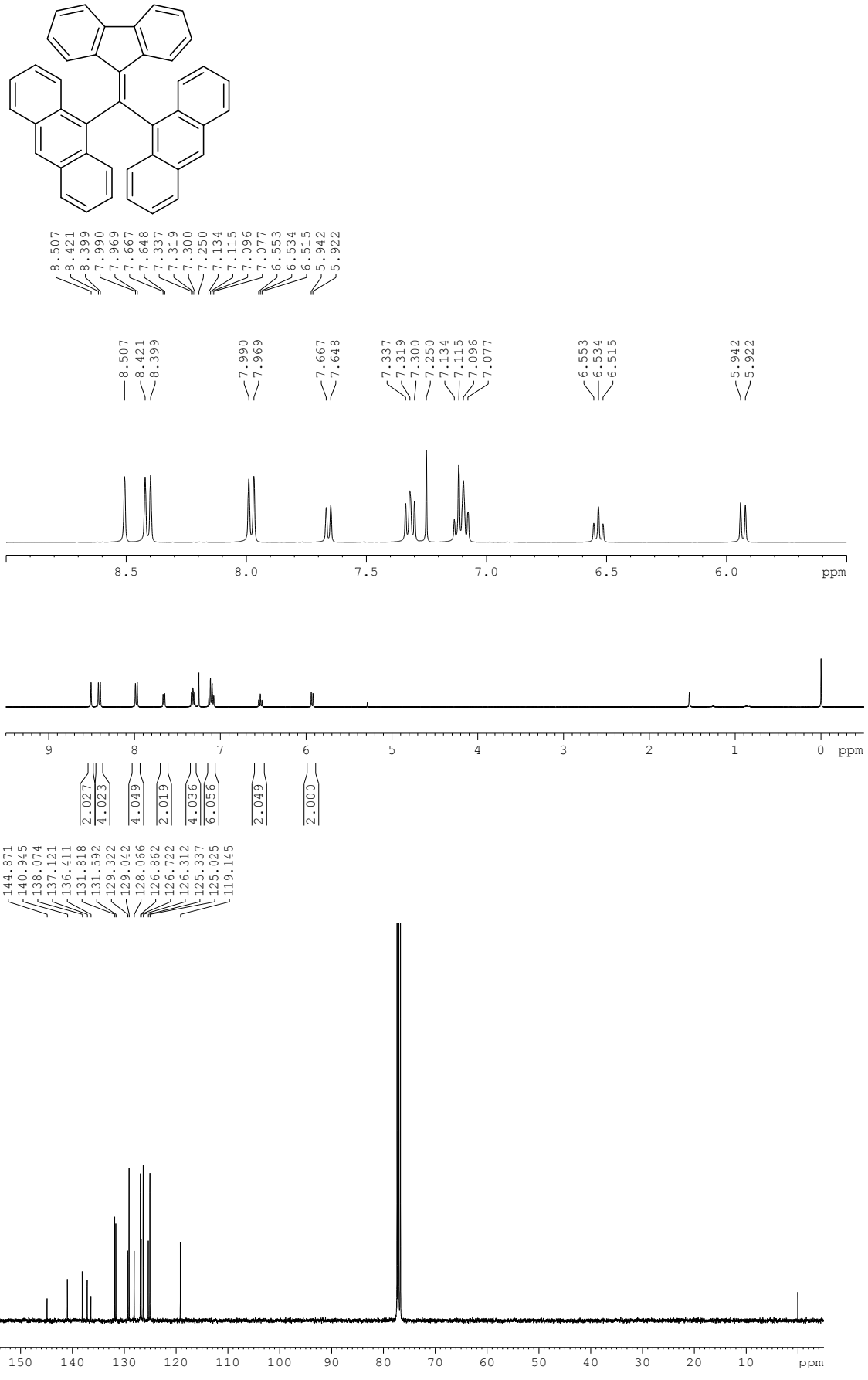


Figure S3 NMR spectra of F-DAn.

3. PL spectrum of F-D in different THF-Water solution.

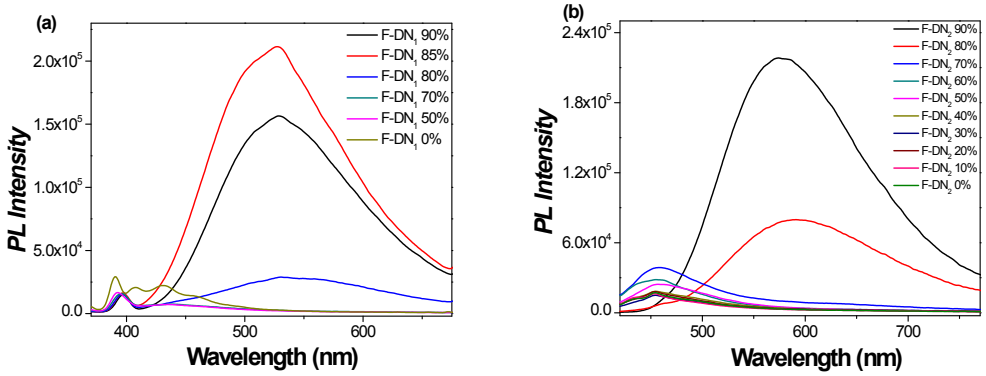


Fig. S4 PL spectra of (a) F-DN_1 and (b) F-DN_2 in different THF-Water solvent mixtures at concentration = 1 x 10^{-5} M.

4. NMR spectra of F-DAn before and after grind.

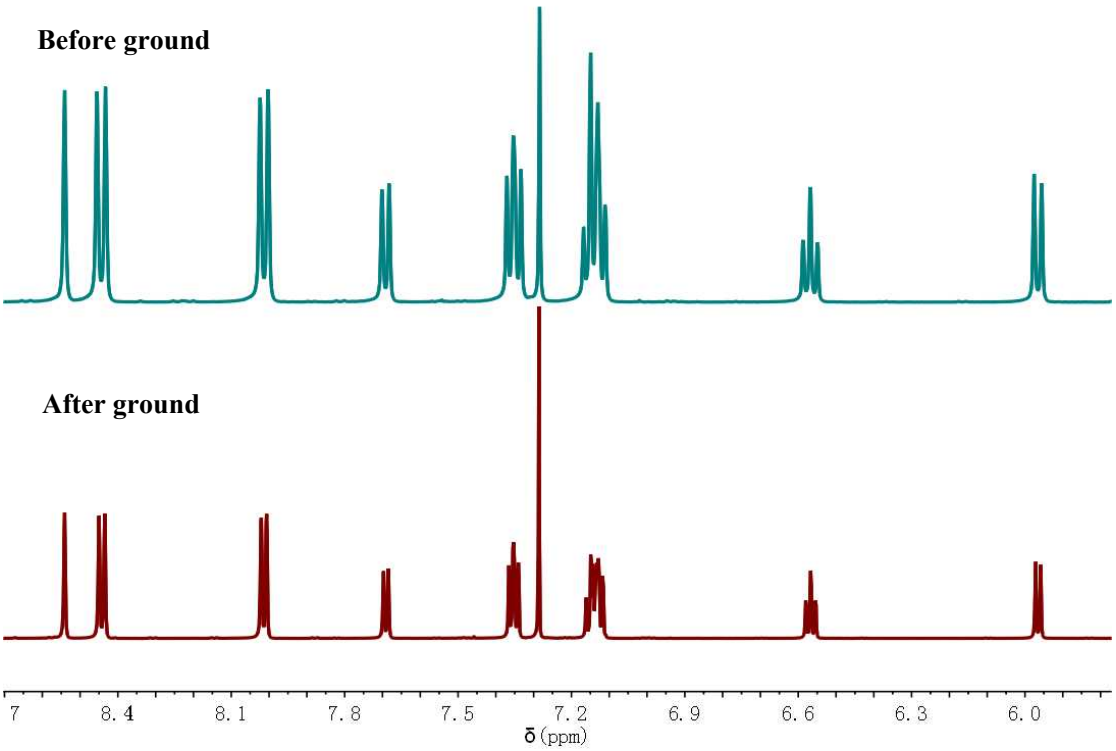


Fig. S5 NMR spectra of F-DAn before and after grind.

5. The fluorescence lifetime of ground sample of F-DAn and solvent fumed F-DAn.

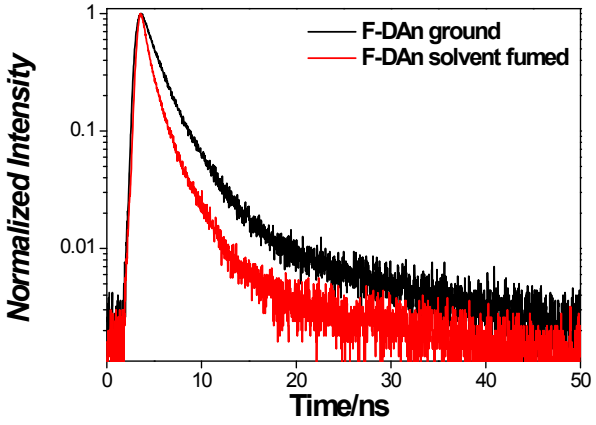


Fig. S6 The fluorescence lifetime of ground sample of F-DAn and solvent fumed F-DAn.

6. The Changes of powder X-ray diffraction (PXRD) patterns before and after ground.

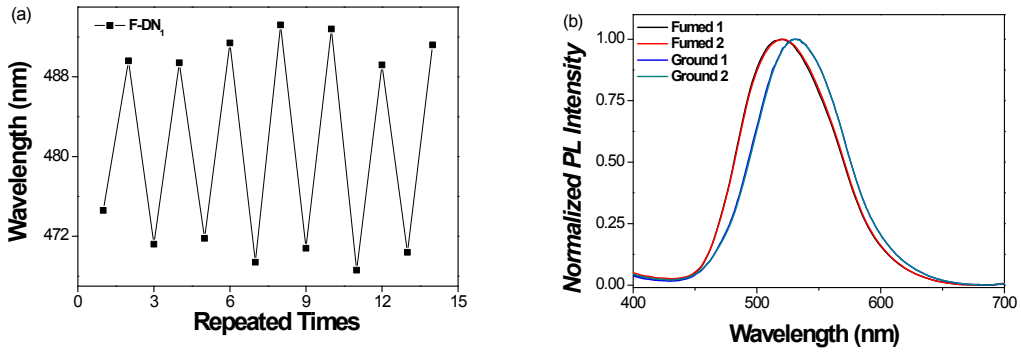


Fig. S7 (a) Cycling behaviors of the emission of F-DN_1 showing the remarkable reversibility. (b) The PL emission spectra of fumed and ground F-DN_2.

7. The alteration of powder X-ray diffraction (PXRD) patterns of F-DN_1 and F-DN_2 before and after ground.

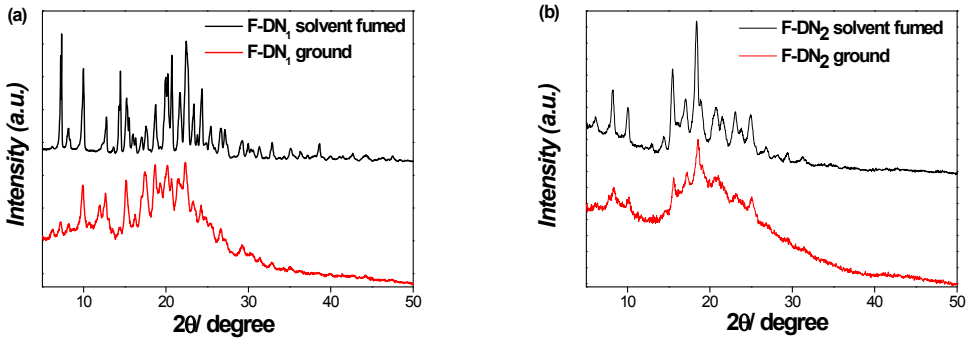


Fig. S8 The alteration of powder X-ray diffraction (PXRD) patterns of (a) F-DN_1 and (b) F-DN_2 by solvent fumed and ground.

8. Crystallographic data

Table S1 Crystallographic data of F-DN_1 and F-DAn

Structure	F-DN_1	F-DAn
temperature (K)	298(2)	296(2)
chemical formula	$C_{34}H_{22}$	$C_{42}H_{26}$
crystal system	monoclinic	monoclinic
space group	*P*2(1)/c	*P*2(1)/c
formula weight	430.52	530.63
a (Å)	12.5099(18)	17.948(3)
b (Å)	13.0134(19)	7.2978(13)
c (Å)	14.188(2)	21.108(4)
α (°)	90	90
β (°)	99.235 (2)	101.866(3)
γ (°)	90	90
V (Å^3)	2279.8(6)	2705.6(8)
D_c(gcm^{-3})	1.254	1.303
F (000)	904	1112
Z	4	4
μ (mm^{-1})	0.071	0.074
R_1,[I > 2σ(I)]	0.0477	0.0472
R_1, (all data)	0.0689	0.0931
ωR_2, [I > 2σ(I)]	0.1320	0.1315
ωR_2, (all data)	0.1525	0.1800
R_{int}	0.0297	0.0415
GOF	1.019	1.046
CCDC number	1010825	1010824

9. ORTEP structures

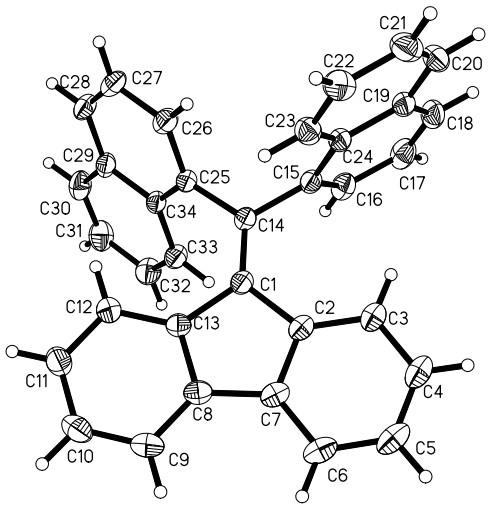


Fig. S9 ORTEP molecular structures of F-DN_1 shown as 50% thermal ellipsoid probability.

A specimen of $C_{34}H_{22}$, approximate dimensions 0.200 mm x 0.200 mm x 0.200 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The integration of the data using a monoclinic unit cell yielded a total of 22795 reflections to a maximum θ angle of 30.00° (0.71 Å resolution), of which 6613 were independent (average redundancy 3.447, completeness = 99.5%, Rint = 2.97%, Rsig = 2.96%) and 4763 (72.02%) were greater than $2\sigma(F^2)$. The final cell constants of a = 12.5099(18) Å, b = 13.0134(19) Å, c = 14.188(2) Å, β = 99.235(2)°, volume = 2279.8(6) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9859 and 0.9859.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 4 for the formula unit, $C_{34}H_{22}$. The final anisotropic full-matrix least-squares refinement on F^2 with 307 variables converged at R1 = 4.77%, for the observed data and wR2 = 15.24% for all data. The goodness-of-fit was 1.019. The largest peak in the final difference electron density synthesis was 0.238 e-/$Å^3$ and the largest hole was -0.231 e-/$Å^3$ with an RMS deviation of 0.043 e-/$Å^3$. On the basis of the final model, the calculated density was 1.254 g/cm^3 and F(000), 904 e-.

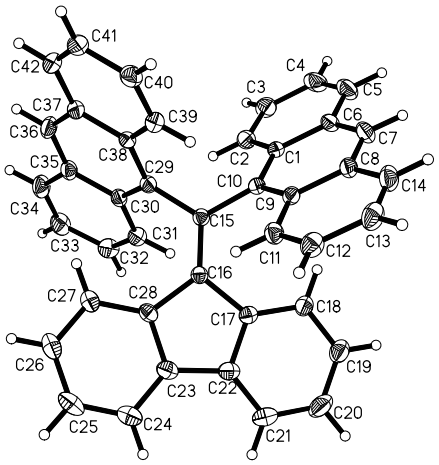


Fig. S10 ORTEP molecular structures of F-DAn shown as 50% thermal ellipsoid probability.

A specimen of $C_{42}H_{26}$, approximate dimensions 0.100 mm x 0.100 mm x 0.200 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The integration of the data using a monoclinic unit cell yielded a total of 16023 reflections to a maximum θ angle of 27.00° (0.78 Å resolution), of which 5884 were independent (average redundancy 2.723, completeness = 99.6%, Rint = 4.15%, Rsig = 5.37%) and 3708 (63.02%) were greater than $2\sigma(F^2)$. The final cell constants of a = 17.948(3) Å, b = 7.2978(13) Å, c = 21.108(4) Å, β = 101.866(3)°, volume = 2705.7(8) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9854 and 0.9927.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 4 for the formula unit, $C_{42}H_{26}$. The final anisotropic full-matrix least-squares refinement on F^2 with 379 variables converged at R1 = 4.72%, for the observed data and wR2 = 18.00% for all data. The goodness-of-fit was 1.046. The largest peak in the final difference electron density synthesis was 0.348 e-/$Å^3$ and the largest hole was -0.367 e-/$Å^3$ with an RMS deviation of 0.113 e-/$Å^3$. On the basis of the final model, the calculated density was 1.303 g/cm^3 and F(000), 1112 e-.

10. Density functional theory (DFT) calculations

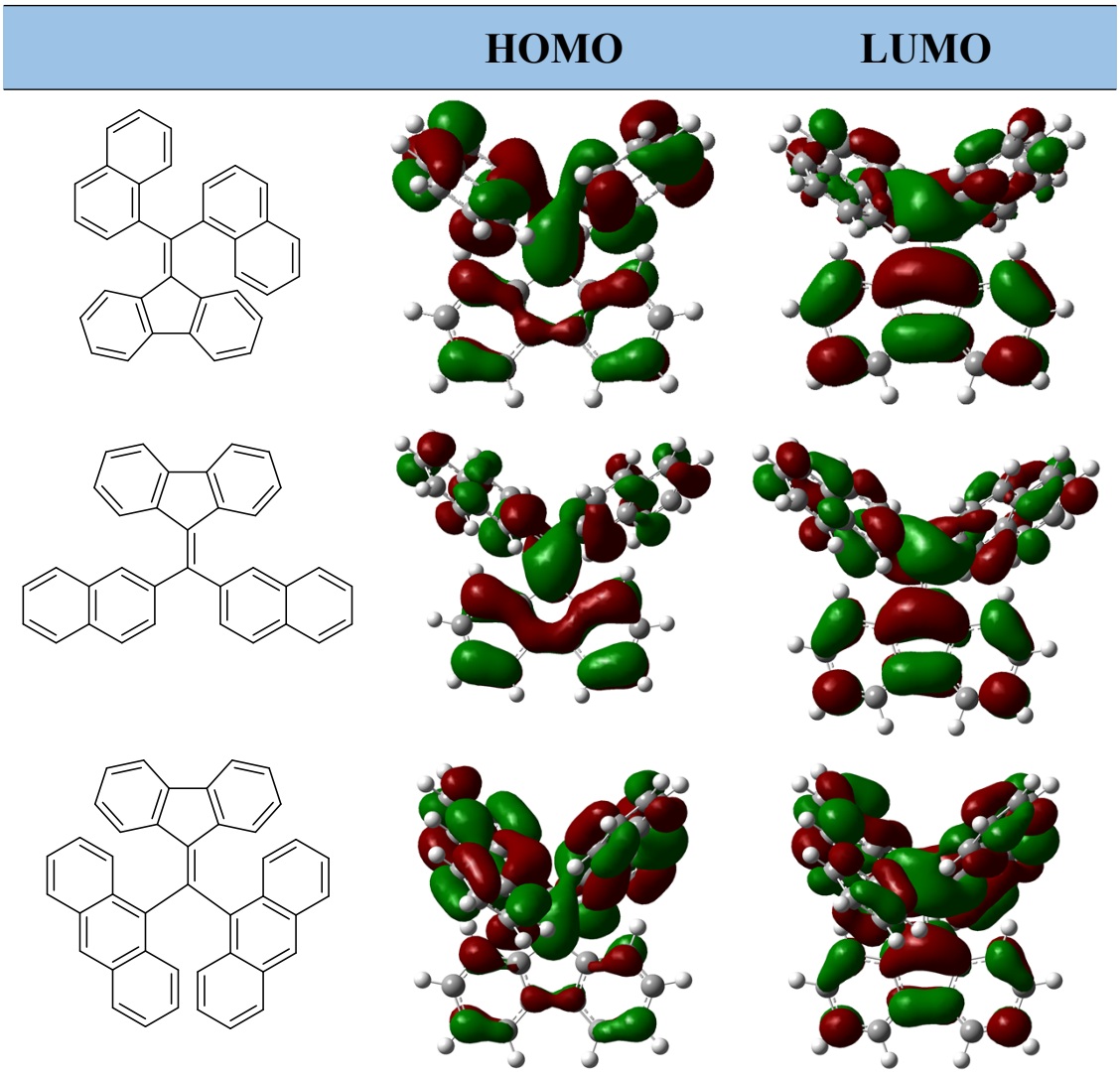


Fig. S11 HOMO-LUMO energy levels of dibenzofulvene derivatives calculated using the B3LYP/6-31G(d) basis set.

11. The pillar-like packing mode in F-DAn.

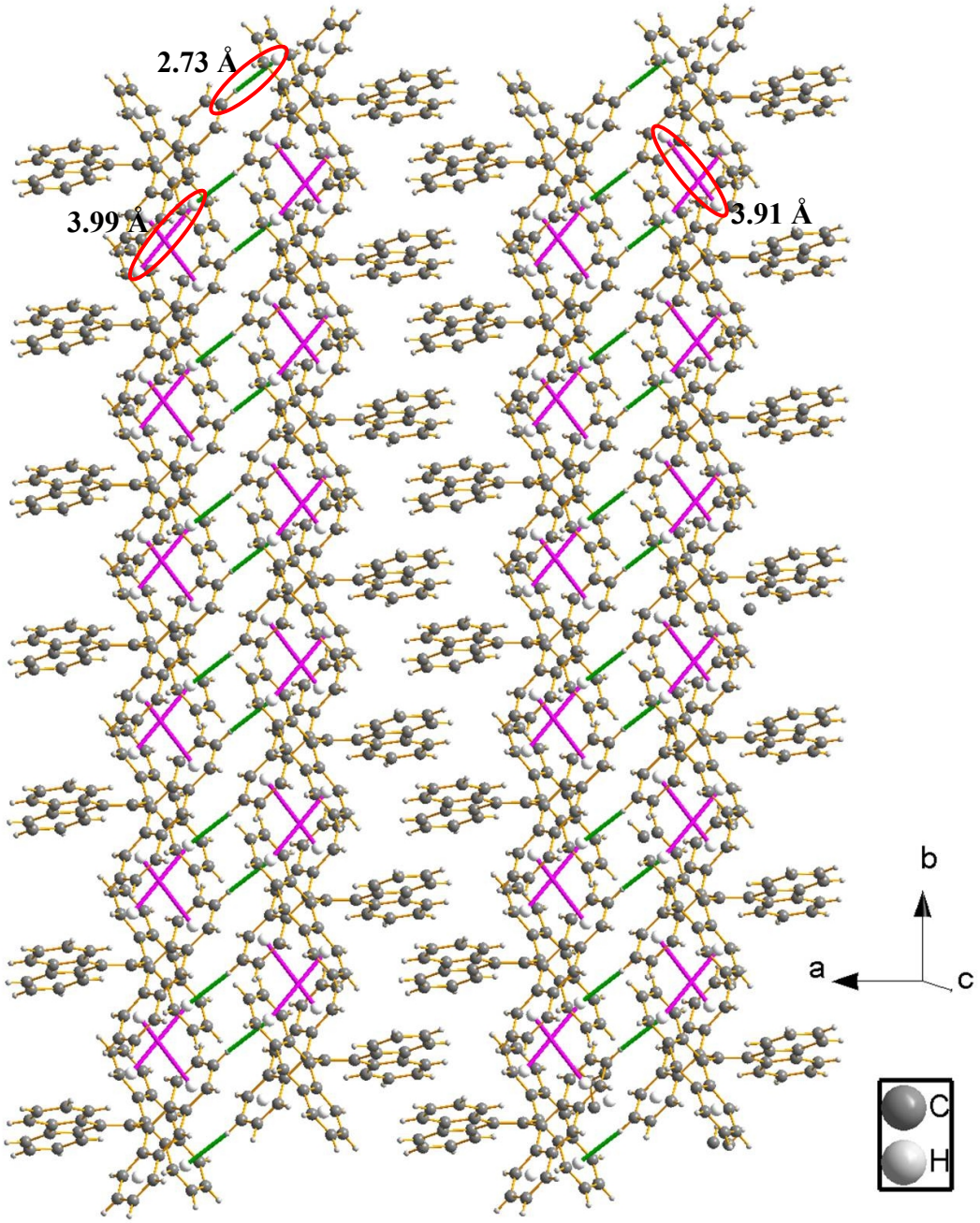


Fig. S12 The pillar-like packing mode in F-DAn.

12. References

1. Spek, A. *J. Appl. Crystallogr.*, 2003, **36,** 7. (b) Spek, A., PLATON, A Multipurpose Crystallographic Tool, Utrecht University The Netherlands, 2006; available *via* http://www.chem.gla.ac.uk /~louis/software/platon/.

2. P. M. Donovan, L. T. Scott, *J. Am. Chem. Soc.*, 2004, **126**, 3108.