C–H···H–C and C–H··· π Contacts Aid Transformation of Dimeric to Monomeric Anthracene in the Solid State

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MATERIALS AND METHODS

All chemicals were obtained from commercial suppliers and used as received without further purification. All reactions were carried out in glassware oven-dried prior to use and wherever necessary, were performed under dry nitrogen in dried, anhydrous solvents using standard gastight syringes, cannulae, and septa. Solvents were dried and distilled by standard procedures. TLC analyses were performed on precoated aluminum plates of silica gel 60 F254 plates (0.25 mm, Merck) and developed TLC plates were visualized under short and long wavelength UV lamps. Flash column chromatography was performed using silica gel of 200-400 mesh employing a solvent polarity correlated with the TLC mobility observed for the substance of interest. Yields refer to chromatographically and spectroscopically homogenous substances. Melting points were obtained using a capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Shimadzu IRPrestige-21 FT-IR spectrometer as neat thin films between NaCl plates in case of liquids and as KBr pellets in the case of solids. ¹H and ¹³C NMR spectra were measured on a 500 MHz Bruker advanced DPX spectrometer. Internal standard used for ¹H and ¹³C NMR is 1,1,1,1-tetramethyl silane (TMS). All CHN analyses were carried out on an Elementar vario MICRO cube Elemental Analyzer. All values recorded in elemental analyses are given in percentages.

Thermal Analysis: Differential scanning calorimetric (DSC) analyses were performed in TA DSC Q20. The experiments were done under nitrogen atmosphere, by applying a heating ramp from 25 to 300 °C with a heating rate of 5 °C/min. The integral under the DSC peak, above the baseline, gives the total enthalpy change for the melting process as given below

$$\int \left\{ \frac{dH}{dt} \right\}_{sample} dt = \Delta H_{sample} \tag{1}$$

Enantiotropic and monotropic phase transition can be understood by applying Burger's theory of heat of transition.¹ Heat of transition theory states that, "if an endothermal transition is observed at some temperature it may be assumed that there is a transition point below it, i. e. the two forms are related enantiotropically and if an exothermal transition is observed at some temperature it may be assumed that there is no transition point below it, i. e. the two forms are related monotropically".

Spectral Measurements: Absorption spectra were recorded on Shimadzu UV-3600 UV-VIS-NIR while fluorescence and excitation spectra were performed on Horiba Jobin Yvon Fluorolog spectrometers respectively. The excitation wavelength used is 350 nm unless otherwise mentioned. Fluorescence lifetime measurements were carried out in an IBH picosecond single photon counting system. The fluorescence decay profiles were de-convoluted using IBH data station software version 2.1, and fitted with exponential decay, minimizing the χ^2 values of the fit to 1 ± 0.05 . All spectroscopic experiments were performed by using standard quartz cuvettes of path length 1cm for solution in dried and distilled solvents. The excitation laser used is 377 nm with a pulse width of less than 100 ps. The solution state fluorescence quantum yields were determined by using optically matched solutions. Quinine sulfate dissolved in 0.5 M H₂SO₄ ($\Phi_{fl} = 0.546$)² is used as the standard. The solid state quantum yield of crystalline AP-I and AP-II was measured using an integrating sphere for which the accuracy was verified using tris(8-hydroxyquinolinate)aluminium (Alq₃) as a standard and is determined to be 0.37 ± 0.04 (reported quantum yield $\Phi_{fl} = 0.40$).³ Radiative (k_{r}) and non-radiative (k_{nr}) decay rate constants can be calculated by using the equations 4 and 5.

$$\Phi = \frac{k_r}{k_r + k_{nr}}$$
(2)
$$\tau_f = \frac{1}{k_r + k_{nr}}$$
(3)
$$k_r = \frac{\Phi}{\tau_f}$$
(4)

$$k_{nr} = \frac{1}{\tau_f} - k_r \tag{5}$$

where Φ_{fl} is the fluorescence quantum yield and τ_f is the fluorescence lifetime. In case of multiexponential decay as in the case of crystalline AP-I and AP-II, the weighted average of the fluorescence lifetime values was used for estimation of rates of radiative and non-radiative processes which could be calculated using equation 6,⁴

$$\tau_f = \frac{\alpha_1 \tau_1^2 + \alpha_2 \tau_2^2 + \alpha_3 \tau_3^2 + \dots}{\alpha_1 \tau_1 + \alpha_2 \tau_2 + \alpha_3 \tau_3 + \dots}$$
(6)

where α = amplitude corresponding to the fluorescence lifetime (τ _f) decay.

X-ray Crystallography: High-quality specimens of appropriate dimensions were selected for the X-ray diffraction experiments. Crystallographic data collected are presented in the supplementary information. Single crystals were mounted using oil (Infineum V8512) on a glass fibre. All measurements were made on a CCD area detector with graphite monochromated Mo K α radiation. The data was collected using Bruker APEXII detector and processed using APEX2 from Bruker. All structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions, but not refined. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97. The full validation of CIFs and structure factors of AP-I and AP-II were performed using the CheckCIF utility and found to be free of major alert level. 3D structure visualization and the exploration of the crystal packing of AP-I and AP-II were carried out using Mercury 3.1.

Frontier Molecular Orbital Analysis: Frontier Molecular Orbitals were obtained by performing DFT calculation using nonlocal hybrid three-parameter Lee-Yang-Parr (B3LYP) level of theory with the (6-311++G**) basis set as implemented in the Gaussian 09W program suite.⁵ Output of the calculations was viewed and analysed using GaussView 5.0.

Quantum Theory of Atoms in Molecules (QTAIM): The wave function for the derivatives AP-I and AP-II were obtained employing the geometries taken from the crystal structure using Gaussian set of codes at B3LYP/6-311++G** level. Quantum theory of atoms in molecules (QTAIM) analysis helps to understand the description of interatomic interaction in the single crystal X-ray structure. A bond is defined along the bond line between two nuclei, called a bond path, along which electron density is concentrated. The bond critical point (BCP) is a point along the bond path at the interatomic surface, where the shared electron density reaches a minimum. The physical characteristics of the BCPs [the electron density at BCP, $\rho(r_{BCP})$, and its Laplacian, $\nabla^2 \rho(r_{BCP})$] reveal the approximate measure of the amount of electron density built up in the bonding region and as such could be taken as characteristic of the bond. When $\nabla^2 \rho(r_{\rm BCP}) < 0$ and is large in magnitude, $\rho(r_{\rm BCP})$ is also large which means that there is a concentration of electronic charge in the internuclear region. This is also an indication of a sharing of electronic charge between both nuclei that defines the covalent (polar) bond. When $\nabla^2 \rho(r_{\text{BCP}}) < 0$ there is a depletion of electronic charge in the internuclear region. Using the AIM 2000 software package, the electron density was integrated over atomic basins according to the quantum theory of atoms in molecules using PROAIM, and thus the BCP data and the molecular graphs were obtained. Existence of bond path and virial path between the adjacent hydrogens (separation distance < 2.4 Å) in the potential energy density map confirms the presence of dihvdrogen contacts.

Hirshfeld Analysis: Important intermolecular interactions within the crystal structure of AP-I and AP-II were identified through Hirshfeld surface analysis using Crystal Explorer 3.0. The Hirshfeld surface is defined as a set of points in 3D space where the ratio of promolecule and procrystal electron densities is equal to 0.5. The exploration of intermolecular contacts is provided by mapping

normalized contact distances (d_{norm}) , which is a function of a closest distance from the point to the nuclei interior (di) and exterior (de) to the surface as well as on the van der Waals radii (r^{vdw}) . 2D fingerprint which were generated by deriving from the Hirshfeld surface by plotting the fraction of points on the surface as the function of *di* and *de* which provide a visual summary of intermolecular contacts within the crystal.

Synthesis Details:



Scheme S1. Synthesis of the dyad AP.

Preparation of 1-(anthracen-9-yl)pyrene: 200 mg (0.78 mmol) of 9-Bromoanthracene⁶ was taken with 20 mL of distilled THF and 10 mL of 2 M K₂CO₃ solution in nitrogen atmosphere and flushed with nitrogen for 15 minutes. 90 mg (0.078 mmol) of Pd(PPh₃)₄ was added and flushed with nitrogen for 10 more minutes. 231 mg of 1-pyreneboronic acid (0.94 mmol) was added and the reaction mixture was refluxed at 65 °C for 12 hours. After the completion of the reaction, reaction mixture was poured into 50 mL of 1N HCl and the product was extracted with dichloromethane. The product was purified using column chromatography using petroleum ether as eluent. 205 mg of pure compound (80 %) was collected as a pale yellow coloured powder m. p. = 250 °C. ¹H NMR (500 MHz, CDCl₃, δ): 8.58 (s, 1H), 8.31 (d, *J* = 3 Hz,1H), 8.16 (m, 3H), 8.06 (m, 2H), 7.96 (m, 2H), 7.72 (d, *J* = 3.6 Hz, 2H), 7.39 (m, 2H), 7.27 (m, 3H), 7.15 (m, 2H) (Figure S12); ¹³C NMR (125 MHz, CDCl₃, δ): 135.34, 133.94, 131.49, 131.31, 131.10, 130.81, 129.39, 128.48, 127.74, 127.69, 127.51, 127.07, 127.04, 126.13, 125.72, 125.63, 125.28, 125.24, 125.18, 124.94, 124.85, 124.71(Figure S13). IR (KBr, cm⁻¹): 3039, 1597, 1440. Elemental analysis: calcd. value for C₃₀H₁₈: 95.21% C, 4.79% H; found: 95.05% C, 4.90% H; *m/z* calculated for C₃₀H₁₈[M]⁺: 378.1409, found: 378.1495.

	Table S1.	Crystall	lograpic	data	of AP-	I and	AP-II.
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	AP-I	AP-II
formula	$C_{30}H_{18}$	$C_{30}H_{18}$
formula wt	378.44	378.44
colour, shape	Ash white	Pale yellow
dimens, mm	0.20x0.15x0.10	0.20x0.15x0.10
crystal system	Orthorhombic	Monoclinic
space group symbol	Iba2	P2(1)/c
No. of formula units, Z	8	4
<i>a</i> , Å	17.0600(14)	7.357(5)
<i>b</i> , Å	29.727(3)	10.583(5)
<i>c</i> , Å	7.9426(6)	25.606(5)
α, deg	90.00	90.00
β, deg	90.00	96.097(5)
γ, deg	90.00	90.00
$V, Å^3$	4028.0(6)	1982.4
temp, K	296(2)	296(2)
dcalcd, g/cm ⁻³	1.369	1.268
no. of reflections	8360	16895

collected		
no. of unique reflections	3455	3499
$2\theta_{\rm max}$, deg	50	50
no. of parameters	271	271
$\begin{array}{c} R1, \ wR2\\ (I > 2\sigma(I)) \end{array}$	0.0477, 0.1091	0.0412, 0.1162
R1, wR2 (all data)	0.1139, 0.1690	0.0579, 0.1370
R factor	4.77	4.13
goodness of fit	1.022	1.091

Table S2. QTAIM analysis of the polymorph AP-I.

Interaction	^a d, Å	${}^{b}\rho_{b}(r), eÅ^{-3}$	$^{c}\nabla^{2}\rho_{b}(r), e\text{Å}^{-5}$				
$H_a - H_b \qquad 2.304 0.005528 \qquad 0.022699$							
$H_c - H_d$ 2.148 0.006764 0.026501							
$C_1 - H_e$ 3.018 0.004220 0.014305							
$C_2 - H_f \qquad 3.186 0.003386 \qquad 0.010359$							
$C_3 - H_g$ 3.389 0.002138 0.006984							
^a <i>d</i> =distance, ^b $\rho_b(r)$ =electron density at the BCP and							
$^{c}\nabla^{2}\rho_{b}(r)$ = Laplacian of the electron density at the BCP							

Table S3. Hirshfeld analyses of AP-I and AP-II.

Interaction ^a	AP-I	AP-II
%С…Н	49.3	45.1
%С…С	1.8	4.5
%Н…Н	48.9	50.4
$ ho^{b}$	27.39	10.02
^a total pe	ercentage	of
intermolecular	r conta	cts ca.
$100\% b\rho = (\%)$	C···H)/(9	‰C···C)]

Table S4. Photophysical properties of AP, AP-I and AP-II.

	λ _{abs} , nm	λ _{fl} , nm	$\tau_{\rm fl},$ ns	$\Phi_{ m fl}$	k_r, s^{-1} x 10 ⁷	k _{nr} , s ⁻¹ x 10 ⁷
APa	320, 340, 370, 390	400-550	4.7	0.8	17	4.30
AP-I ^b	300-440	410, 420, 460	4.3 (30%), 0.8 (70%) ^c 6.4 (75%), 1.6 (25%) ^d	0.3	9.26	21.60

AP-II ^b 300-4	80 420, 520, 560	1.8 (82%), 5.0 (18%) ^e 6.4 (27%), 90 (52%) ^f 4.2 (08%), 96 (92%) ^g	0.4	0.42	0.63
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^achloroform solution; ^bcrystalline state; monitored at ^c420 nm; ^d470 nm; ^e420 nm; ^f520 nm and ^g560 nm; abs – absorption; fl – fluorescence



Figure S1. ¹H NMR spectra of AP in CDCl₃; inset shows expansion between 7 to 8.6 δ .



Figure S2. ¹³C NMR spectra of AP in CDCl₃; inset shows expansion between 124 to 136 δ .



Figure S3. Crystal packing of A) AP-I; B) AP-II.



gure S4. C–H··· π interactions between A) nearest PY units ; B) nearest AN units and C) C-H···H-C interaction between AN units in AP-I.



Figure S5. QTAIM electron density map of AP-I; arrows indicate the C-H····H-C contacts.



Figure S6. A) C–H··· π interaction between AN and PY; B) π - π interaction between the PY units in AP-II.



Figure S7. Hirshfeld 2D fingerprint plot of A) AP-I and B) AP-II.



Figure S8. Differential scanning calorimetric analysis of AP-I and AP-II; inset shows the AP-II to AP-I transition at 233°C.



Figure S9. Absorption spectra of AN, PY, dyad AP and the sum of AN and PY in chloroform solution.



Figure S10. Steady state emission spectra of AN, PY and dyad AP in chloroform solution.



Figure S11. Steady state emission spectra of A) AP-I and B) AP-II, excited at different wavelengths 300, 350 and 400 nm.



Figure S12. Frontier molecular orbital diagram of AP-I and AP-II obtained using DFT calculations (B3LYP/6-311++G**).



Figure S13. Fluorescence decay profile of AP-II, excited at 377 nm and monitored at 560 nm.



Figure S14. Steady state emission spectrum of A) AP-I before and after the exposure to hexane vapour; B) AP-II before and after the exposure to ethyl acetate vapour; C) AP-I before and after the exposure to ethyl acetate vapour; D) AP-II before and after the hexane vapour. Insets show the corresponding images.



Figure S15. PXRD pattern of A) AP-I; B) AP-I After exposing to hexane vapour; C) AP-II; D) AP-II after exposing to ethyl acetate vapour.

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