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Regio-selective substitution at the 1,3- and 6,8-positions of pyrene for the construction of small dipolar molecules

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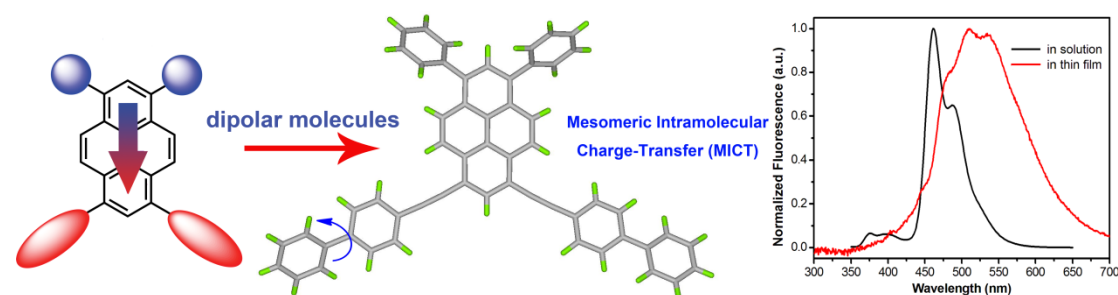
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ABSTRACT: This article presents a novel asymmetrical functionalization strategy for the construction of dipolar molecules *via* efficient regio-selective functionalization along Z-axis of pyrene at both the 1,3- and 6,8-positions. Three asymmetrically substituted 1,3-diphenyl-6,8-R-disubstituted pyrenes were fully

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4 characterized by X-ray crystallography, photophysical properties,
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6 electrochemistry, and DFT calculations.
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9 **Introduction**

10 The construction of dipolar molecules with donor-acceptor (D-A) type structures
11 are of interest given their potential application in organic optoelectronic devices.¹
12
13 Such dipolar architectures can, *via* a suitable choice of the D/A units, fine-tune the
14
15 electron redistribution, facilitate simultaneous manipulation of the HOMO-LUMO
16
17 energy gap and the emission color by intramolecular charge transfer (ICT),² control
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19 crystallinity,³ and be used to self-assemble molecular morphologies.⁴
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28 Pyrene⁵ belongs to a family of polycyclic aromatic hydrocarbons (PAHs) with a
29
30 natural electron-donating and an electron-accepting role.⁶ Apart from other PAHs
31
32 such as anthracene,⁷ fluorene,⁸ pyrene possess the equivalent activity of the sites at
33
34 the 1-, 3-, 6- and 8-positions, it is different to develop an effectively rational synthetic
35
36 strategy to asymmetric functionalization of pyrene. Typically, tetrabromopyrene and
37
38 pyrene tetraone derivatives as key precursor were extensively utilized in the
39
40 construction of PAHs for semiconductor applications, *via* the introduction of terminal
41
42 moieties.^{5,9} Up to date, few examples on pyrene chemistry focus on constructing
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44 “push-pull” system and investigating the effect of the electron-donating/accepting
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46 strength to emission color of dipolar molecules, and the region-chemical relationship
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48 between donor and acceptor units.
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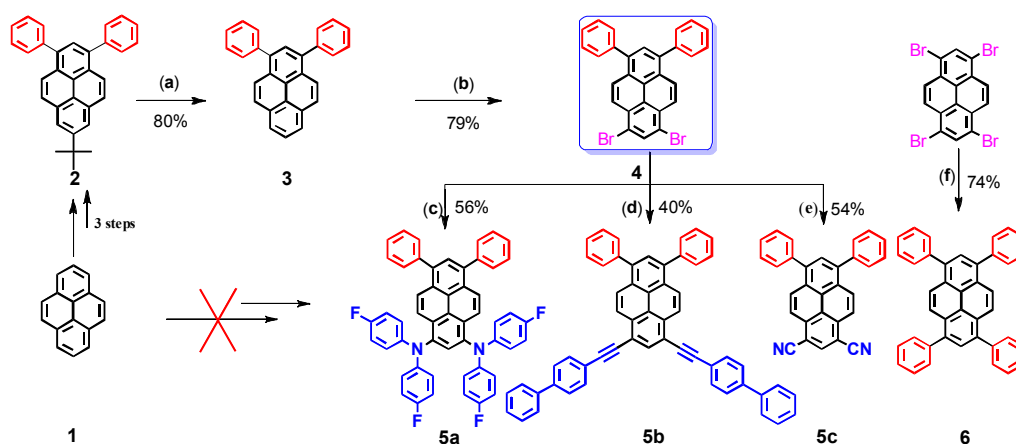
57 Recently, Kim group and Lee group developed a set of tetrakisubstituted pyrenes
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59 functionalized with electron-donor and electron-acceptor moiety located at 1,6- and
60

1
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4 3,8-positions randomly in nature, respectively.¹⁰ However, reports focus on
5
6
7 regio-selective substituted pyrene derivatives for bipolar materials are scant, due to
8
9
10 the lack of straightforward strategies to modify the pyrene core. Müllen *et al.* reported
11
12 the selective asymmetric functionalization of pyrene at the K-region for use in organic
13
14 field-effect transistors *via* a two step chemical functionalization.¹¹ Meanwhile,
15
16
17 Bodwell *et al.* reported a regioselective synthesis of 4,5-dialkoxy-1,8-dibromopyrenes
18
19 for preparing 1,8-pyrenylene-ethynylene macrocycles.¹² After that, a series pyrene
20
21 derivatives with D-A substituents of pyrene derivative in the K-region was presented
22
23 as follows.¹³ Very recently, both strong donors and acceptors were introduced into the
24
25
26 K-region and the 2,7-positions respectively, via 2,7-dibromo- and 2,7-diiodopyrene-
27
28
29 4,5,9,10-tetraones as the key intermediates.¹⁴ Such novel synthetic procedures at the
30
31
32 pyrene core not only greatly enrich our knowledge of synthetic chemistry, but also
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35 stimulate further research into semiconductor materials.
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39 Unlike the previously mentioned studies, our interest stems from exploring new
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42 effective strategies for preparing asymmetric substituted pyrene along the Z-axis to be
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45 used in high-performance electroluminescence material applications. Previously, we
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48 have released a novel approach for modifying both at the 1-, 3- and 4-, 5-, 9-,
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51 10-positions using classical methods from 1,3-dibromo-7-*tert*-butylpyrene in
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54 considerable yield,¹⁵ in this case, a *tert*-butyl group plays a role for protecting the ring
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56
57 against electrophilic attack at the 6- and 8-positions.¹⁶ Herein, we further present a
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59
60 novel synthetic strategy to realize regio-selective substitution at the 1,3- and
6,8-positions of pyrene for the construction of dipolar molecules,

Results Discussion sections

Assuming that the *tert*-butyl group can be removed by an effective approach, the effective approach to regio-selective substitution at the 1,3- and 6,8-positions of pyrene would be achievable. Based on our knowledge, the bulky *tert*-butyl group can be removed by using Nafion-H as catalyst.¹⁷ Following this inspiration, the 1,3-diphenylpyrene (**3**) was successfully synthesized in 85 % yield from 7-*tert*-butyl-1,3-diphenylpyrene, which is a key step for building dipolar architectures along the Z-axis.¹⁸ The detailed synthetic procedure is illustrated in Scheme 1. Further bromination of **3** afforded 1,3-dibromo-6,8-diphenylpyrene (**4**) in high yield (79 %).¹⁹ Compound **4** is a novel bromide precursor used for synthesizing the desired dipolar architectures (**5**). This is the first example for the regio-selective, stepwise, and asymmetric substitution of pyrene at the active 1,3-, and 6,8-positions. Compared with along short axis (4,5,9,10-position) or at 2,7-positions, introduces dipole to pyrene as well, asymmetric functionalization both at 1,3-positions and 6,8-positions of pyrene show potential advantages, a) more artificial dipolar molecules pyrene-based would be synthesized from bromopyrene intermediations by Pd-catalyzed; b) introduce the substitutions at 1,3,6,8-positions would lead to a special influence on both the $S_2 \leftarrow S_0$ and $S_1 \leftarrow S_0$ transition^{18,19} compared with other substitution pattern, c) this strategy is beneficial to tune the band gap of the dipolar architectures to realize color control by introducing the substitution groups. For comparison, 1,3,6,8-tetraphenylpyrene (TPPy, **6**)²⁰ was synthesized.



Scheme 1. Synthetic route for the preparation of **5** and **6**. (a) Nafion-H, *o*-xylene, 160 °C, 24 h, (b) BTMABr₃ (benzyltrimethylammonium tribromide), CH₂Cl₂/MeOH, room temp., 12 h, (c) NHPH₂F, Pd(OAc)₂/(*t*Bu)₃P/K₂CO₃, *o*-xylene, 160 °C, 24 h, (d) 4-Ethynyl-1,1'-biphenyl, [PdCl₂(PPh₃)₂], CuI, PPh₃, Et₃N/DMF (1:1), 48 h, 100 °C, (e) CuCN, NMP, 48 h, 180 °C, (f) phenylboronic acid, toluene, Pd(PPh₃)₄, K₂CO₃, 90 °C, 24 h.

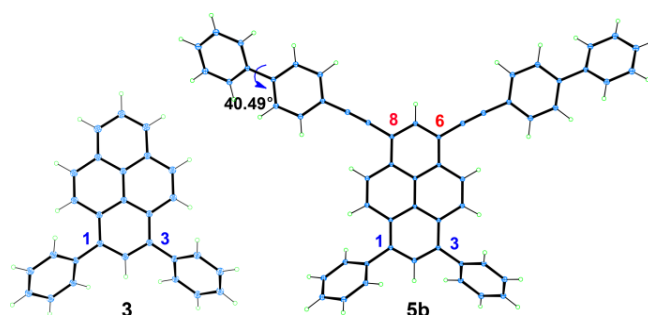


Figure 1. X-ray structures of molecules **3** and **5b**

Suitable single crystals were obtained by slow evaporation of CH₂Cl₂/hexane solvent for **2**,¹⁶ **5b** (CCDC 1025083) and **6** (CCDC 1025084), CH₂Cl₂/acetone for **3** (CCDC 1025085) at RT. The crystal structures are presented in Figure 1 and the supporting information. Generally, the packing of the structures, and the molecular

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4 conformation in the crystal were influenced by short intermolecular interactions or the
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6 π -stacking present. For instance, the phenyl moieties located at the pyrene
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8 1,3-positions in **2**, are all twisted with torsion angles in the range 45–65° relative to
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10 the pyrene plane; which is arranged in a herringbone motif with a slip angle of 28°;¹⁶
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12 molecules of **3** are held together by strong face-to-face $\pi\cdots\pi$ stacking interactions with
13
14 a shortest separation of 3.31 Å; the dipolar molecule **5b** exhibited a π -stacked packing
15
16 motif with π - π distances in the range 3.38–3.51 Å; but no $\pi\cdots\pi$ stacking was observed
17
18 in **6** (see SI). Interestingly, **5b** is remarkably planar with a twist angle of
19
20 approximately 40.49(3)° between the adjacent rings of the biphenyl moiety, which is
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22 consistent with reported values.²¹ The intriguing conformations of the dipolar
23
24 molecules can also lead to special optical properties.

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26 The effect on the photophysical properties of a series of 1,3-diphenyl-
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28 6,8-donor/acceptor asymmetrically substituted pyrenes **3**, **5** and **6** are discussed.
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30 Figure 2 exhibits the absorption spectra of **3**, **5** and **6** in dilute dichloromethane. In the
31
32 D- π -A type molecules, with a strong -NPh₂F donor in **5a**, the absorption spectra
33
34 exhibited a weak but broad band in the low energy absorption (375-400 nm), which
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36 indicated a charge-transfer (CT) excitation between the donor and acceptor moieties.
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38 For **5b**, a broad band around 332 nm is mainly due to a localized π - π^* excitation of
39
40 the biphenylethynyl group with high extinction coefficients ($\epsilon = 48400 \text{ mol}^{-1} \text{ cm}^{-1} \text{ L}$).
41
42 In contrast, the strong acceptor group -CN in **5c** has a strong influence on both the S₁
43
44 \leftarrow S₀ and S₂ \leftarrow S₀ excitations, consistent with the large extinction coefficients with
45
46 oscillator strengths. However, the compounds **3** and **6** exhibited a similar absorption
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pattern with little influence on both the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ excitation, as reflected in the similar extinction coefficients (Table 1). Obviously, with an electron withdrawing group asymmetrically substituted at the 6,8-positions, the $S_1 \leftarrow S_0$ excitation has high extinction coefficients, while the electron donors play a significant role in influencing both the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ excitation by lowering the extinction coefficients.

Table 1. The photophysical and electrochemical properties of compounds **3**, **5** and **6**.

R	$\lambda_{(S_1 \leftarrow S_0)}^a / \epsilon$ nm / M ⁻¹ cm ⁻¹ L	$\lambda_{(S_2 \leftarrow S_0)}^a / \epsilon$ nm / M ⁻¹ cm ⁻¹ L	$\lambda_{\text{max Abs}}^b$ (nm)	$\lambda_{\text{max PL}}$ (nm)	Stokes shift nm	Φ_f^c	HOMO ^c (IP) ^d (eV)	LUMO (eV)	Energy gap (eV)
3	357 (28000)	286 (41000)	359	396 ^a (462) ^b	39 (103)	0.27 ^a (0.03) ^b	-5.14 (-5.83)	-1.58 ^e (-2.76) ^f	3.56 ^c (3.07) ^g
5a	433 (18500)	285 (27000)	438	488 (469)	55 (31)	0.92 (0.42)	-4.84 (-5.70)	-1.88 (-3.15)	2.97 (2.55)
5b	437 (12900)	332 (48400)	455	462 (510)	25 (55)	0.90 (0.44)	-4.93 (-5.77)	-2.12 (-3.24)	2.80 (2.53)
5c	411 (46100)	296 (41000)	425	456 (537)	45 (112)	0.96 (0.32)	-5.90 (---)	-2.69 (---)	3.21 (2.69)
6	394 (29500)	304 (41200)	400	421 (464)	27 (64)	0.87 (0.52)	-5.01 (-5.76)	-1.69 (-2.93)	3.32 (2.83)

^a Measured in dichloromethane at room temperature. ^b As a thin film. ^c DFT/B3LYP/6-31G* using Gaussian. ^d determined using AC-3. ^e LUMO = Eg+HOMO. ^f LUMO (eV) = Eg - IP, ^g Calculated from λ_{edge} in thin film. dotted line: IP>6.2eV.

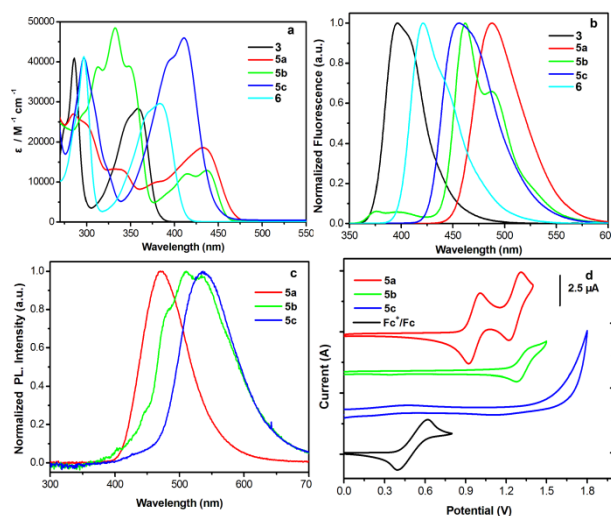


Figure 2. (a) Absorption (b) fluorescence spectra of **3**, **5** and **6** in CH₂Cl₂, (c) PL spectra and (d) cyclic voltammograms of **5**.

The emission maxima of **3**, **5** and **6** were in the range of 396-488 nm in dilute dichloromethane solution with a systematic bathochromic shift following the order **3**<**6**<**5c**<**5b**<**5a**, suggesting that the energy gap could be fine-tuned between the ground and excited states by choosing the substituent group. The fluorescence of **5a**

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4 exhibited pronounced positive solvatochromism with an
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6 intramolecular-charge-transfer (ICT) state, in which the emission wavelength display
7
8 a large red shift from 464 (in cyclohexane) to 503 (in DMF) (see SI); whereas the
9
10 D- π -A conjugated compound **5b** displayed a maximum emission peak at 462 nm with
11
12 a shoulder at 488 nm, and contributed to an efficient mesomeric
13
14 intramolecular-charge-transfer (MICT) emission, due to a twist angle (40.49(3) $^\circ$) of
15
16 the Franck–Condon vertical state between the diphenyl moieties.²² The dipolar
17
18 molecule **5** exhibits solvent dependency of the spectroscopic and photophysical
19
20 properties. The linear relationship of the Stokes shift (ΔV_{st}) against the solvent
21
22 parameters (ϵ , n) of **5** were determined by a Lippert–Mataga plot.¹⁶ Obviously, the
23
24 MICT of the solvent polarity dependence of the fluorescence bands is weaker than for
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26 the TICT case (See SI).
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36 Compounds **5b** and **5c** as films exhibited green emission and displayed a $\lambda_{film\ max}$ at
37
38 510 nm and 537 nm, respectively, which is significantly red shifted relative to their
39
40 solutions due to the planar structure of the molecule which tends to form dimers.
41
42 However, the maximum of **5a** was blue-shifted by 19 nm compared with
43
44 measurement in solution, due to the presence of the bulky electron-donor $-NPh_2F$
45
46 moiety which not only plays a role in suppressing aggregation in solid, but also
47
48 affects the conformation of the electronic structures, so can tune energy gap.
49
50 Additionally, in solution, the dipolar molecules **5** have similar PL quantum yields ($>$
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52 0.90), suggesting displays excited state ICT character. The red shifted emission with
53
54 decreased quantum yields of **5** (0.32–0.44) in the solid state attribute to the π - π
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stacking interactions. Whereas **3**, both in solution and in thin films, exhibited the lowest PL efficiencies, attributed to the strong molecular aggregation.

The electrochemical properties of **5** were investigated by cyclic voltammetry (CV). The oxidation of **5a** and **5b** displayed a quasi-reversible oxidation process with HOMO energy levels of 5.15 eV and -5.51 eV, respectively. For compound **5c**, the oxidation wave was not clearly observed owing to the presence of the strongly electron-withdrawing -CN group. The result was further confirmed by photoelectron spectroscopy. The ionization potential of **3**, **5a**, **5b** and **6** are measured in thin film, and IP = 5.83, 5.70, 5.77 and 5.76 eV (Table 1). However, in the presence of the strong electron withdrawing group -CN in **5c**, the maximum IP range was greater than the instrument full-scale (6.2 eV). The optical gap of the **3**, **5** and **6** were calculated from the absorption spectra of their thin films at 3.07, 2.55, 2.53, 2.69 and 2.83 eV, respectively.

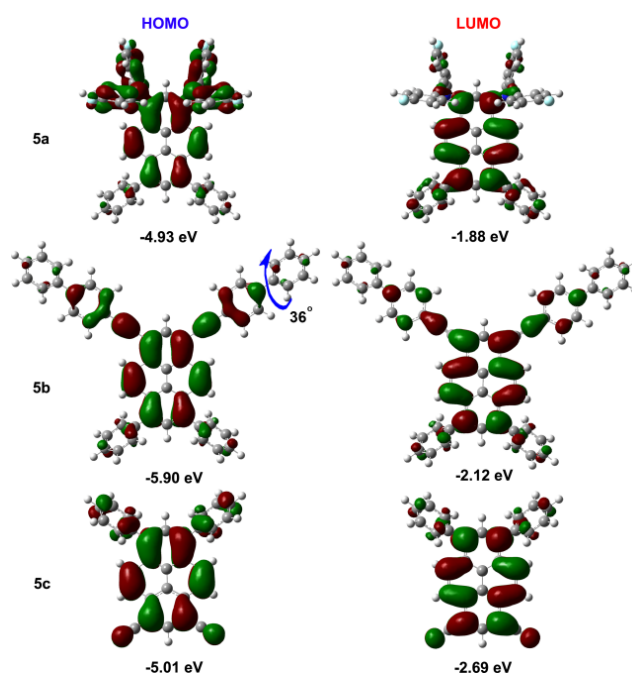


Figure 3. Computed molecular orbital plots (B3LYP/6-31G*) of **5a-c**.

The energy gap was further evaluated by density functionalized theory (DFT)

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4 calculations. As shown in Figure 3, Obviously, due to the substituents asymmetrically
5 located at the 1,3- and 6,8-positions, the HOMO of **5a** mainly spread over the -NPh₂F
6 moiety and the pyrene ring, whereas the LUMO extended on pyrene core and
7 fragment phenyl ring, respectively, which implies a partial charge separation between
8 donor (-NPh₂F moiety) and acceptor (phenyl moiety); for **5b**, the HOMO and LUMO
9 were delocalized in the pyrene moiety; However, with strong acceptor -CN in **5c**, the
10 HOMO located at entire molecular skeleton and the LUMO mostly existed at pyrene
11 and cyano group. Obviously, the ICT states would be formed in molecular **5a** and **5c**
12 along Z-axi with a strong donor at 1,3-positions and an acceptor at 6,8-positions. The
13 calculated HOMO-LUMO gap of **5** is 2.97, 2,81 and 3,21 eV. In addition, the fully
14 optimized structure of **5b** is shown to exhibit a twist angle for C21-C22-C25-C26 of
15 36°, very close to the X-ray structure.
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35 36 **Conclusion**

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38 In summary, a facile synthetic strategy for the construction of dipolar
39 architectures was explored, in which the asymmetric unit including phenyl
40 rings and NPh₂F/biphenylethynyl/CN moieties are introduced into the
41 1,3-positions and 6,8-positions along the Z-axis of the pyrene core by
42 regio-selective substitution. X-ray analysis has confirmed the novel asymmetric
43 substitution of the pyrene core. The small dipolar molecules pyrene-based
44 compounds possess fine ICT state between D-A units in the ground state. This
45 article presents a revolutionary methodology for the functionalization of the
46 pyrene core and has potential application in organic photonics.
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Experimental Section

General: All melting points are uncorrected. ^1H / ^{13}C NMR spectra were recorded on a FT- NMR spectrometer (300 MHz and 400MHz), respectively and referenced to 7.26 and 77.0 ppm for chloroform-D solvent with SiMe_4 as an internal reference: J -values are given in Hz. IR spectra were measured for samples as KBr pellets in a FT-IR spectrophotometer. Mass spectra were obtained with a Mass Spectrometer at 75 eV using a direct-inlet system. UV/Vis spectra were obtained with a UV/Vis/NIR spectrometer in various organic solvents. Fluorescence spectroscopic studies were performed in various organic solvents in a semimicro fluorescence cell (Hellma[®], 104F-QS, 10×4 mm, 1400 μL) with a spectrophotometer. Fluorescence quantum yields were measured using absolute methods. Differential scanning calorimeter (DSC) was performed under nitrogen atmosphere at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. Photoluminescence spectra were obtained using a luminescence spectrometer. Ionization potential was determined by atmospheric photoelectron spectroscopy. Electrochemical properties of HOMO levels were determined by Electrochemical Analyzer. The cyclic voltammetry was carried out in 0.10 M tetrabutylammonium perchlorate in anhydrous dichloromethane and THF with a scan rate of 100 mV s^{-1} at room temperature. The quantum chemistry calculation was performed on the Gaussian 03W (B3LYP/6-31G* basis set) software package. Crystallographic data of titled compound were collected by graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) in the ω scan mode. Data (excluding structure factors) on the structures reported here have been deposited with the Cambridge Crystallographic Data Centre

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2
3
4 with deposition numbers. CCDC 1025083-1025085 contain the supplementary
5
6
7 crystallographic data for this paper. These data can be obtained free of charge from
8
9 The Cambridge Crystallographic Data Centre via
10
11 www.ccdc.cam.ac.uk/data_request/cif.
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13

14
15 **Film preparation:** The thin films were prepared by solution process. Dissolve 10 mg
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17 sample in 1 mL toluene solution, the solution is placed on the substrate, which is then
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19 rotated at high speed in order to spread the fluid by centrifugal force.
20
21

22
23 **Material:** Unless otherwise stated, all other reagents used were purchased from
24
25 commercial sources and were used without further purification. The preparations of
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27 2-*tert*-butylpyrene (**1**)²³ and 7-*tert*-butyl-1,3-dibromopyrene (**2**)¹⁶ were described
28
29 previously.
30
31

32 33 **Synthesis of 7-*tert*-butyl-1,3-diphenylpyrene (2)**

34
35 A mixture of 7-*tert*-butyl-1,3-dibromopyrene (**1**) (200 mg, 0.5 mmol), phenylboronic
36
37 acid (250 mg, 2.0 mmol) in toluene (12 mL) and ethanol (4 mL) at room temperature
38
39 was stirred under argon, and K₂CO₃ (250 mg, 1.8 mmol) and Pd(PPh₃)₄ (70 mg, 0.06
40
41 mmol) were added. After the mixture was stirred for 30 min at room temperature
42
43 under argon, the mixture was heated to 90 °C for 24 h with stirring. After cooling to
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45 room temperature, the mixture was quenched with water, extracted with CH₂Cl₂ (2 ×
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47 30 mL), washed with water and brine. The organic extracts were dried with MgSO₄
48
49 and evaporated. The residue was purified by column chromatography eluting with
50
51 (CH₂Cl₂/hexane, 1:1) to give **2** as white prisms (CH₂Cl₂/hexane, 1:2) (124 mg, 63 %).
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60 M.p. 186 °C; IR (KBr): ν_{\max} = 2958, 2900, 2866, 1766, 1597, 1484, 1462, 1442, 1396,

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4 1360, 1227, 1151, 875, 837, 810, 764, 702, 613, 503, 457 cm^{-1} ; ^1H NMR (300 MHz,
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6
7 CDCl_3): $\delta_{\text{H}} = 1.59$ (s, 9H, *t*Bu), 7.44–7.69 (m, 10H, Ar-*H*), 7.94 (s, 1H, pyrene-*H*₂),
8
9 8.01 (d, $J = 9.2$ Hz, 2H, pyrene-*H*_{4,10}), 8.18 (d, $J = 9.2$ Hz, 2H, pyrene-*H*_{5,9}), 8.20 ppm
10
11 (s, 2H, pyrene-*H*_{6,8}); ^{13}C NMR(75 MHz, CDCl_3): $\delta = 149.2, 141.1, 137.1, 131.2,$
12
13 130.6, 129.0, 128.3, 127.8, 127.6, 127.2, 125.3, 125.1, 123.4, 122.2, 35.2, 31.9 ppm;
14
15 MS: m/z 410.2 [M]⁺; elemental analysis calcd. (%) for $\text{C}_{32}\text{H}_{26}$ (410.2): C 93.62, H
16
17 6.38; found: C 93.81, H 6.19.

22 23 **Synthesis of 1,3-diphenylpyrene (3)**

24
25 A mixture of 1,3-diphenyl-7-*tert*-butylpyrene (**2**) (410 mg, 0.09 mmol), Nafion-H
26
27 (400 mg), and *o*-xylene (4 mL) were refluxed for 24 h, and then cooled to room
28
29 temperature. The solid was removed *in vacuo* and the mother solution collected. The
30
31 crude product was purified by column chromatography using hexane as eluent to
32
33 afford a yellow solid (300 mg, 85 %). M.p. 136.5–137.2 °C. ^1H NMR (300 MHz,
34
35 CDCl_3): $\delta = 7.45$ –7.50 (m, 2H, Ar-*H*), 7.53–7.58 (m, 4H, Ar-*H*), 7.66–7.68 (m, 4H,
36
37 Ar-*H*), 8.00 (d, $J = 8.8$ Hz, 2H, pyrene-*H*), 8.05 (d, $J = 2.9$ Hz, 2H, pyrene-*H*), 8.16, (s,
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39 1H, pyrene-*H*), 8.20 (d, $J = 2.9$ Hz, 2H, pyrene-*H*) and 8.22 (s, 1H, pyrene-*H*) ppm;
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60
 ^{13}C NMR (100 MHz, CDCl_3): $\delta = 141.01, 137.30, 131.28, 130.65, 129.35, 128.40,$
127.93, 127.46, 127.32, 126.13, 125.27, 125.16 and 124.98 ppm. FABMS: m/z :
354.22 (M^+). $\text{C}_{28}\text{H}_{18}$ (354.44): calcd C 94.88, H 5.12; found: C 94.85, H 5.11.

55 56 **Synthesis of 1,3-dibromo-6,8-diphenylpyrene (4)**

57
58 To a mixture of 1,3-diphenylpyrene **3** (300 mg, 0.85 mmol) in dry CH_2Cl_2 (30 mL)
59
60 was added dropwise a solution of BTMABr₃ (benzyltrimethylammonium tribromide)

1
2
3
4 (1.0 g, 2.6 mmol) in CH₂Cl₂ (10 mL) and methanol (5 mL) at 0 °C for 1 h under argon
5
6
7 atmosphere. The resulting mixture was allowed to slowly warm up to room
8
9
10 temperature and stirred overnight. The reaction mixture was poured into ice-water (60
11
12 mL) and neutralized with an aqueous 10 % Na₂S₂O₃ solution. The mixture solution
13
14
15 was extracted with dichloromethane (2 × 20 mL). The organic layer was washed with
16
17
18 water (2 × 20 mL) and saturated brine (20 mL), then the solution was dried (MgSO₄)
19
20
21 and condensed under reduced pressure. The crude compound was washed with hot
22
23
24 hexane to afford pure 1,3-dibromo-6,8-diphenylpyrene **3** (330 g, 79 %) as a yellow
25
26
27 solid. M.p. 184–186°C. ¹H NMR (400 MHz, CDCl₃): δ = 7.49 (m, 2H, Ar-*H*),
28
29
30 7.53–7.57 (m, 4H, Ar-*H*), 7.62–7.67 (m, 4H, Ar-*H*), 8.03 (s, 1H, pyrene-*H*), 8.29 (d, *J*
31
32 = 9.2 Hz, 2H, pyrene-*H*), 8.33 (d, *J* = 9.6 Hz, 2H, pyrene-*H*) and 8.49 (s, 1H,
33
34
35 pyrene-*H*) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 140.41, 138.61, 133.60, 130.58,
36
37
38 130.47, 129.29, 128.45, 127.91, 127.61, 127.17, 127.10, 125.70, 124.30 and 119.24
39
40
41 ppm. FABMS: *m/z*: 510.05 (M⁺). C₂₈H₁₆Br₂ (512.23): calcd C 65.65, H 3.15; found: C
42
43
44 65.35, H 3.34.

44 **Synthesis of 1,3-bis[di(4-fluorophenyl)amino]-6,8-diphenylpyrene (5a)**

45
46
47 The corresponding 1,3-dibromo-6,8-diphenylpyrene (150 mg, 0.29), bis(4-fluoro-
48
49
50 phenyl)amine (180 mg, 0.87 mmol), Pd(OAc)₂ (40 mg, 0.18 mmol), (*t*-Bu)₃P (0.05
51
52
53 mL), sodium *tert*-butoxide (200 mg, 2.05 mmol), and toluene (10 mL) were mixed
54
55
56 together and heated at 120 °C for 24 h. The reaction was quenched with water (30 mL)
57
58
59 and the organic layer taken into 100 mL of CH₂Cl₂, washed with brine solution, and
60
dried over MgSO₄. Evaporated of the solvent under vacuum resulted in a solid residue.

1
2
3
4 The residue was adsorbed in silica gel and purified by column chromatography using
5
6 hexane as eluent and recrystallization from ethyl acetate to afford the corresponding
7
8 desired compound **5a** as green powder (125 mg, 56 %); M.p. 161.1–162.5 °C. ¹H
9
10 NMR (400 MHz, CDCl₃): δ = 6.84–6.94 (m, 20H, Ar-*H*), 7.40–7.44 (m, 2H, Ar-*H*),
11
12 7.49 (t, *J* = 7.4 Hz, 8H, Ar-*H*), 7.53 (s, 1H, pyrene-*H*), 7.56 (d, *J* = 7.2 Hz, 8H, Ar-*H*),
13
14 7.94 (s, 1H, pyrene-*H*), 8.00 (d, *J* = 9.6 Hz, 2H, pyrene-*H*) and 8.03 (d, *J* = 9.6 Hz, 2H,
15
16 pyrene-*H*) ppm; ¹³C NMR (100 MHz, CDCl₃) δ = 159.27, 156.86, 144.67, 144.65,
17
18 141.56, 140.63, 137.89, 130.47, 129.97, 128.48, 128.34, 128.04, 127.40, 126.55,
19
20 125.60, 123.19, 123.11, 122.80, 116.07 and 115.85 ppm. FABMS: *m/z*: 760.31 (M⁺).
21
22 C₅₂H₃₂F₄N₂ (760.82): calcd C 82.09; H 4.24, N 3.68; found: C 82.16, H 4.39 N 3.55.
23
24
25
26
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31 **Synthesis of 1,3-bis[(3-biphenyl)ethynyl]-6,8-diphenylpyrene (5b)**

32
33 Mixture of 1,3-dibromo-6,8-diphenylpyrene (50 mg, 0.10 mmol), PdCl₂(PPh₃)₂ (21
34
35 mg, 0.03 mmol), CuI (10 mg, 0.05 mmol), PPh₃ (20 mg, 0.08 mmol), and
36
37 4-ethynyl-1,1'-biphenyl (53 mg, 0.30 mmol) was added into a degassed solution of
38
39 triethylamine (5 mL) and *N,N*-dimethylmethanamide (5 mL) under argon atmosphere.
40
41
42 The resulting mixture was stirred at 100 °C for 48 h. After cooling to room
43
44 temperature, the mixture was quenched with water, extracted with CH₂Cl₂ (2 × 30
45
46 mL), washed with water and brine. The organic extracts were dried with MgSO₄ and
47
48 evaporated. The residue was purified by column chromatography eluting with
49
50 (CH₂Cl₂/hexane, 2:1) to give **5b** as dark yellow powder (CH₂Cl₂/hexane, 1:2) (28 mg,
51
52 40 %). M.p. 263.1–264.9 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.39 (m, 1H, Ar-*H*),
53
54 7.49 (m, 5H, Ar-*H*), 7.58 (m, 5H, Ar-*H*), 7.65–7.71 (m, 13H, Ar-*H*), 7.77 (d, *J* = 8.2
55
56
57
58
59
60

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3
4 Hz, 4H, Ar-*H*), 8.06 (s, 1H, pyrene-*H*), 8.38 (d, $J = 9.3$ Hz, 2H, pyrene-*H*), 8.50 (s,
5
6
7 1H, pyrene-*H*), 8.67 (d, $J = 9.3$ Hz, 2H, pyrene-*H*); ^{13}C NMR (100 MHz, CDCl_3) $\delta =$
8
9
10 141.92, 141.19, 140.64, 140.31, 140.06, 138.57, 133.31, 132.90, 132.08, 131.98,
11
12 130.67, 129.96, 128.87, 128.41, 128.11, 127.82, 127.66, 127.51, 127.13, 127.07,
13
14 127.00, 125.43, 122.22, 120.60, 117.65, 95.38 and 88.72 ppm. FABMS: m/z : 706.33
15
16
17 (M^+). $\text{C}_{56}\text{H}_{34}$ (706.87): calcd C 95.15, H 4.85; found: C 95.07, H 5.03.

20 Synthesis of 1,3-dicyano-6,8-diphenylpyrene (5c)

21
22
23 A mixture of 1,3-dibromo-6,8-diphenylpyrene (**2**) (100 mg, 0.20 mmol), CuCN (42
24
25 mg, 0.49 mmol), and *N*-methyl-2-pyrrolidone (10 mL) for 24 h, and then cooled to
26
27 room temperature. The solid was removed *in vacuo* and the mother solution collected.
28
29
30 the water was added into the solution and extracted with CH_2Cl_2 (2×30 mL), washed
31
32 with water and brine. The organic extracts were dried with MgSO_4 and evaporated.
33
34
35 The residue was purified by column chromatography eluting with (CH_2Cl_2 /hexane,
36
37 4:1) to give **5c** as yellow powder (43 mg, 54 %). M.p. up to 300 °C. IR: ^1H NMR (400
38
39 MHz, CDCl_3): $\delta = 7.56\text{--}7.67$ (m, 10H, Ar-*H*), 8.24 (s, 1H, pyrene-*H*), 8.50 (d, $J = 9.6$
40
41 Hz, 2H, pyrene-*H*), 8.56 (s, 1H, pyrene-*H*), 8.63 (d, $J = 8.8$ Hz, 2H, pyrene-*H*); ^{13}C
42
43 NMR (100 MHz, CDCl_3) $\delta = 141.95, 139.34, 135.60, 133.55, 131.94, 131.44, 130.71,$
44
45 128.76, 128.33, 127.41, 124.34, 123.69, 123.58, 117.11 and 105.60 ppm. FABMS:
46
47 m/z : 404.35 (M^+). $\text{C}_{30}\text{H}_{16}\text{N}_2$ (404.46): calcd C 89.09, H 3.99; N, 6.93; found: C 89.19,
48
49 H 3.69; N, 6.53.

57 Synthesis of 1,3,6,8-tetraphenylpyrene (6)

58
59
60 1,3,6,8-tetrabromopyrene (200 mg, 0.386 mmol), phenylboronic acid (254 mg, 2.08

1
2
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4 mmoL), and Pd(PPh₃)₄ (50 mg, 0.04 mmoL) and aqueous 2.0 M NaOH (2 mL) were
5
6
7 mixed in a flask containing with argon saturated toluene (10 mL). The reaction
8
9
10 mixture was stirred at 90 °C for 20 h. After it was cooled to room temperature, the
11
12 reaction mixture was extracted with dichloromethane (40 mL × 2). The combined
13
14 organic extracts were dried with anhydrous MgSO₄ and evaporated. The crude
15
16 product was purified by column chromatography using hexane/dichloromethane (1:4)
17
18 as eluent to provide a pale powder and recrystallized from hexane to afford
19
20 1,3,6,8-tetraphenylpyrene **6** as light yellow powder (146 mg, 74 %). M.p
21
22 300.1–301.8 °C. ν_{\max} (KBr)/cm⁻¹ 2952, 1608, 1513, 1494, 1459, 1286, 1245, 1176,
23
24 1106, 1035, 835, 549 and 476. ¹H NMR (400 MHz, CDCl₃): δ = 7.43–7.47 (m, 2H,
25
26 Ar-*H*), 7.53 (t, *J* = 7.6 Hz, 8H, Ar-*H*), 7.66 (d, *J* = 8.0 Hz, 8H, Ar-*H*), 8.00 (s, 2H,
27
28 pyrene-*H*) and 8.17 (s, 4H, pyrene-*H*) ppm; ¹³C NMR (100 MHz, CDCl₃) δ = 141.04,
29
30 137.22, 130.613, 129.498, 128.31, 128.10, 127.26, 125.91 and 125.28 ppm. FABMS:
31
32 *m/z*: 506.30 (M⁺). C₄₀H₂₆ (506.63): calcd C 94.83, H 5.17; found: C 94.77, H 5.29.
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42 ASSOCIATED CONTENT

43 Supporting Information

44
45 For crystallographic data in CIF, ¹H/¹³C NMR data and spectral data for all new
46
47 compounds etc. This material is available free of charge via the Internet at
48
49 <http://pubs.acs.org>.
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Notes

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