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PAPER

Highly emissive hand-shaped π-conjugated alkynylpyrenes: Synthesis, structures, and photophysical properties†

Jian-Yong Hu,*[a,b] Xin-Long Ni,[a] Xing Feng,[a] Masanao Era,[a] Mark R. J. Elsegood,[c] Simon J. Teat[d] and Takehiko Yamato*[a]

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Three alkynyl-functionalised, hand-shaped, highly fluorescent and stable emitters, namely, 2-*tert*-butyl-4,5,7,9,10-pentakis(*p*-R-phenylethynyl)pyrenes have been successfully synthesized *via* a Pd/Cu-catalysed Sonogashira cross-coupling reaction. The chemical structures of the alkynylpyrenes were fully characterized by their $^1H/^{13}C$ NMR spectra, mass spectroscopy and elemental analysis. Synchrotron single-crystal X-ray analysis revealed that there is a 1-D, slipped, face-to-face motif with off-set, head-to-tail stacked columns, which are clearly influenced by the single, bulky, *tert*-butyl group in the pyrene ring at the 2-position. Detailed studies on the photophysical properties in both solutions and thin films strongly indicate that they might be promising candidates for optoelectronic applications, such as organic light-emitting devices (OLEDs) or as models for investigating the fluorescent structure–property relationship of the alkynyl-functionalised pyrene derivatives.

Introduction

Recently, carbon-rich organic compounds with a high degree of π-conjugation have attracted great attention due to their interesting optoelectronic properties as ideal materials in modern electronic and optoelectronic devices.[1–3] Generally, the optoelectronic effects of these organic π-conjugated compounds are highly dependent on their molecular structure design. Major issues for the organic π-conjugated compounds used in electronic and optoelectronic devices are their ability to form morphologically stable and homogeneous films, and excellent efficiencies with respect to high quantum yields, charge-carrier transport, *etc.* To fulfil these and other requirements, several families of organic π-conjugation compounds with interesting molecular architectures have been exploited. Among them, alkynyl-functionalised banana-shaped,[4] cruciform-shaped,[5] as well as star-shaped[6] π-conjugated fluorophores are of particular interest because they exhibit unique optical and electronic properties deriving from their individual multiply-conjugated pathway structures. The representative examples of the banana-shaped fluorophores are the oligo(arylene ethynylene)s of Yamaguchi *et al.*,[4] the cruciform-shaped 1,2,4,5-tetra-substituted(phenylethynyl) benzenes of Haley *et al.*,[5a] and the star-shaped hexaethynylbenzene derivatives of Vollhardt *et al.*[6a]

Pyrene is one of the most important large π-conjugated aromatics, which has high fluorescence quantum yield in solution and shows efficient excimer emission.[7] Pyrene and its derivatives have been widely used as photophysical probes,[8] as liquid crystalline materials,[9] as well as in photonic devices.[10] Despite its wide uses, the fact that the absorption and emission properties of the pyrene core are confined to the UV region, remains a major drawback. Recently, several alkynyl-functionalised pyrenes have been fully studied where the introduction of alkynyl groups induced effective extension of the π-conjugation into the visible region and a large increase in fluorescence intensity.[11] For example, Ziessel and co-workers reported two acetylene-linked dendrimers by combining ethynylphenylaminoacyls with pyrene cores and studied their liquid crystal and gel properties in optoelectronic devices.[11e] Hence, there exist more intensive interests in developing new alkynylpyrenes as model systems or promising candidates for practical uses in optoelectronic devices.

As a part of our research program on the construction of pyrene-based extended π-conjugation compounds,[12] we recently reported a series of alkynyl-functionalised, cruciform-shaped light-emitting monomers, which revealed highly pure-blue

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[a] *Department of Applied Chemistry, Faculty of Science and Engineering, Saga University, Honjo machi 1, Saga-shi, Saga, Japan. E-mail: yamatot@cc.saga-u.ac.jp; Fax: +81-952-288548*
[b] *Department of Organic Device Engineering, Yamagata University, Yonezawa, Yamagata992-8510, Japan. E-mail: hujianyong@yz.yamagata-u.ac.jp; Fax: +81-238-263412*
[c] *Chemistry Department, Loughborough University, Loughborough, Leicestershire, UK, LE11 3TU*
[d] *Advanced Light Source, Berkeley Lab., 1 Cyclotron Road, Berkeley, CA94720, USA*

† Electronic supplementary information (ESI) available: $^1H/^{13}C$ NMR spectra of **4a–c** and **6**, TGA curves of **4a–c** and **6**, cyclic voltammogram (CV) of **4a–c** and **6**, the effect of concentration on the fluorescence emission spectra of **4c**, and photoluminesence (PL) spectra of **4a–c** in 1 wt %-doped into PMMA films. CCDC reference number 811807. For ESI and crystallographic data in CIF format see DOI: 10.1039/c2ob06865f

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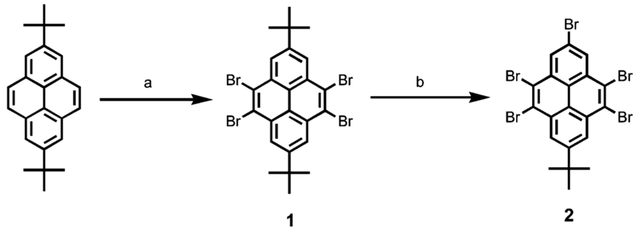
emissions, high fluorescence quantum yields, and a low degree solid-state π-aggregation. These properties are completely attributed to the bulky *tert*-butyl groups substituted in the pyrene ring at the 2- and 7-positions.[12b] Along this line, in this paper, we present the synthesis, structures and photophysical properties of three alkynyl-functionalised π-conjugated emitters of 2-*tert*-butyl-4,5,7,9,10-pentakis(*p*-R-phenylethynyl)pyrenes. We investigated the single-crystal X-ray structures and also the photophysical properties of the pyrenes in solution and thin films. Although these newly synthesized compounds differ from the former cruciform-shaped emitters, in which the two bulky *tert*-butyl groups played the key roles in suppressing the π-aggregations of pyrene units both in solution and in solid-states,[12b] we surmised that the single *tert*-butyl group at the 2-position would also play an important role in the molecular arrangement and orientation in solution and the solid-state, which might lead to interesting optoelectronic properties.

Results and discussion

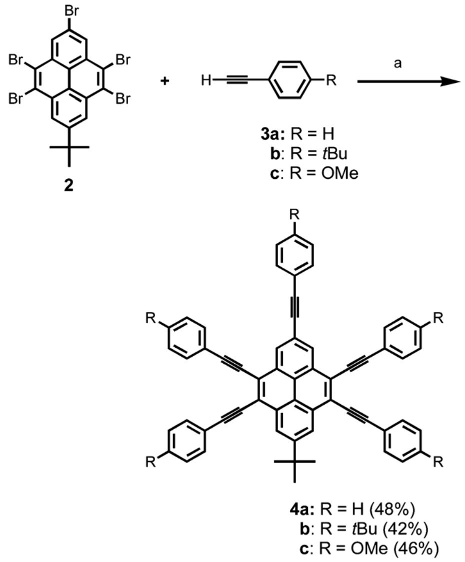
Synthesis and characterization

Following our previously reported approach, we readily obtained the intermediate 4,5,9,10-tetrabromo-2,7-di-*tert*-butylpyrene **1** by the Lewis acid-catalysed bromination of 2,7-di-*tert*-butylpyrene.[13] Interestingly, when the reaction time was prolonged to 8 h, the Lewis acid-catalysed *ipso*-bromination of the tetrabromide **1** took place, affording the pentabromide **2** in high yield of 85% (Scheme 1), and it served as the starting material for the synthesis of the 4,5,7,9,10-pentakis(*p*-substituted phenylethynyl)pyrene derivatives.

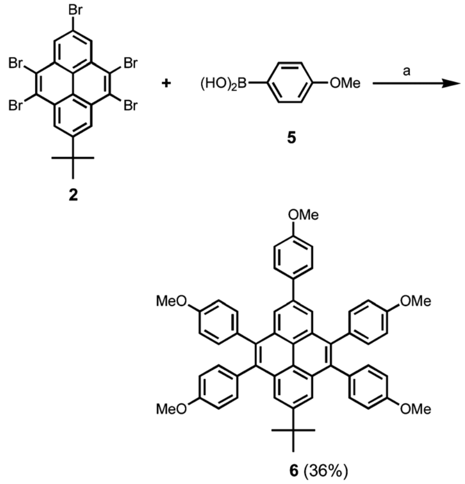
We carried out the modified Sonogashira cross-coupling reaction of the pentabromide **2** with various kinds of phenylacetylenes **3**, and succeeded in producing the corresponding 2-*tert*-butyl-4,5,7,9,10-pentakis(*p*-substituted phenylethynyl)pyrenes **4** in good yields (recrystallization yields) (Scheme 2). As a comparison, we prepared a non-conjugated pyrene **6**, [2-*tert*-butyl-4,5,7,9,10-pentakis(4-methoxyphenyl)pyrene] by the standard Suzuki cross-coupling reaction[14] (Scheme 3).



Scheme 1 Synthesis of 4,5,7,9,10-pentabromo-2-*tert*-butylpyrene (**2**). Reagents and conditions: (a) Br_2, Fe-powder, CH_2Cl_2, rt 4 h, 90% (**1**). (b) Br_2, Fe-powder, CH_2Cl_2, rt 8 h, 85% (**2**).



Scheme 2 Synthesis of 2-*tert*-butyl-4,5,7,9,10-pentakis(phenylethynyl)pyrene derivatives **4a–c**. Reagents and conditions: (a) $[PdCl_2(PPh_3)_2]$, CuI, PPh_3, Et_3N/DMF (1 : 1), 24–48 h, 100 °C.



Scheme 3 Synthesis of 2-*tert*-butyl-4,5,7,9,10-pentakis(4-methoxyphenyl)pyrene (**6**). Reagents and conditions: (a) $[Pd(PPh_3)_4]$, Na_2CO_3, toluene/EtOH, 24 h, 70 °C, 36%.

We fully determined the molecular structures and purities of these new pyrenes **4** and **6** by ^1H NMR spectra, FT-IR spectroscopy, mass spectroscopy, as well as elemental analysis. All results were consistent with the proposed hand-shaped structures (see ESI†). All compounds are soluble in common organic solvents, such as CH_2Cl_2, $CHCl_3$, tetrahydrofuran (THF), and toluene. Thermal properties of **4** and **6** were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements. The decomposition temperatures (T_d) of the pyrenes **4** and **6** were in the range of 433–507 °C corresponding to a 5% weight loss. No glass transition temperatures (T_g) of these pyrenes **4** and **6** were detected in the DSC measurements, and the melting points of **4a–c** were in the range of 315–383 °C except for **6**, which shows no melting point. The key thermal data of the pyrenes **4** and **6** are listed in Table 2.

X-Ray molecular structure and crystal packing of 4c

The performance of the organic compounds in optoelectronic devices strongly relies on the intermolecular order in the active layer. We further confirmed the molecular structure of **4c** by

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Table 1 Summary of the crystal data of **4c**

Parameter	**4c**
Empirical formula	$C_{65}H_{48}O_5\cdot 0.07CH_2Cl_2$
Formula weight (g mol^{-1})	914.80
T/K	100(2)
Wavelength (Å)	0.7749
Crystal system	Triclinic
Space group	$P\bar{1}$
Crystal color and size (mm)	Yellow, 0.25 × 0.03 × 0.02
a/Å	10.0392(8)
b/Å	15.7261(12)
c/Å	16.0211(11)
α (°)	81.677(5)
β (°)	82.511(5)
γ (°)	79.608(6)
Volume (Å^3)	2447.5(3)
Z	2
Density, calcd. (g m^{-3})	1.241
Absorption coefficient (mm^{-1})	0.101
F(000)	962
θ range for data collection	2.48 to 25.59
Reflections collected	16532
Independent reflections	6986
Observed data ($F^2 > 2\sigma(F^2)$)	4579
R_{int}	0.0373
Restraints/parameters	0/645
Goodness-of-fit on F^2	1.035
R_1 ($F^2 > 2\sigma(F^2)$)	0.0723
wR_2 (all data)	0.2097

synchrotron single-crystal X-ray analysis.[15] The yellow, needle-shaped crystals were obtained by slow evaporation of a of mixture concentrated $CHCl_3/CH_2Cl_2$ solutions. The crystallographic data for this compound are summarized in Table 1. Structure diagrams of **4c** are shown in Fig. 1. There is one complete molecule and a small amount of CH_2Cl_2 (see structure refinement details†) in the asymmetric unit. The ten ethynyl carbons are essentially coplanar with the central pyrene ring. Two C_6H_4 rings are close to being co-planar with the central pyrene ring with C(41) > C(46) and C(59) > C(64) twisted by 0.8 and 6.1° respectively, while three are substantially twisted with C(23) > C(28), C(32) > C(37) and C(50) > C(55) twisted by 31.7, 47.3 and 30.4° respectively. The crystal packing diagrams of **4c** are shown in Fig. 2. The molecules adopt a 1-D slipped face-to-face motif with off-set head-to-tail stacked columns. Each **4c** molecule displays 24-point π–π stacking with molecules above and below using both the pyrenyl and ethynyl carbons,[12b] with intermolecular distances of *ca.* 3.42–3.58 Å.[16] As we expected, the individual stacking arrangement in the current crystal of **4c** is clearly influenced by the single, bulky, *tert*-butyl group in the pyrene ring at the 2-position. Thus, these newly developed alkynylpyrenes with unique intermolecular interactions suggests that they might be advantageous to high charge-carrier transport in optoelectronic device applications.[17]

Photophysical and electrochemical properties

We measured the UV/Vis absorption spectra of these new alkynylpyrenes **4** both in dilute CH_2Cl_2 solutions and in thin neat films at room temperature, and the results are presented in Table 2, together with those of the non-conjugated pyrene **6**. The normalized UV/Vis absorption spectra of **4** and **6** in solution and in thin neat films are shown in Fig. 3. For the non-conjugated pyrene **6**, the absorption spectra reveal a vibronic feature that is characteristic of the unsubstituted parent 2,7-di-*tert*-butylpyrene with a short wavelength absorption maximum at *ca.* 290 nm, and a long wavelength absorption maximum at *ca.* 355 nm, indicating the five introduced 4-methoxyphenyl groups are only slightly conjugated to the central pyrene core. This is also observed in the 1,3,6,8-tetraarylpyrenes.[18] Interestingly, for the hand-shaped alkynylpyrenes **4**, although the profiles of the optical absorption spectra are similar to those of our previously reported cruciform-shaped alkynylpyrenes,[12b] red-shifts by *ca.* 25 nm in each spectrum were observed, which are attributed to the additional phenylacetylenic substituents attached at the 7-position. On the other hand, the longest wavelength bands of the alkynylpyrenes **4** are largely red-shifted by *ca.* 100 nm, located at 433 nm for **4a**, 438 nm for **4b**, and 443 nm for **4c**, with respect to those of the parent pyrene[19] (λ_{abs} = 336 nm in CH_2Cl_2) and **6**, respectively. This can be attributed to the increased conjugation length arising from the introduction of the five phenylacetylenic units. In particular, **4c** displayed the largest bathochromic shift due to the strongest electron-donating ability of the methoxy group.[12b] In the case of thin neat films, for **6**, compared to the corresponding spectrum in solution, a small bathochromic shift (~2 nm) was observed in the UV/Vis absorption spectrum, which indicates that this compound exhibited a very similar conformation in both states.[20] However, for the alkynylpyrenes **4a–c**, the UV/Vis absorption spectra completely

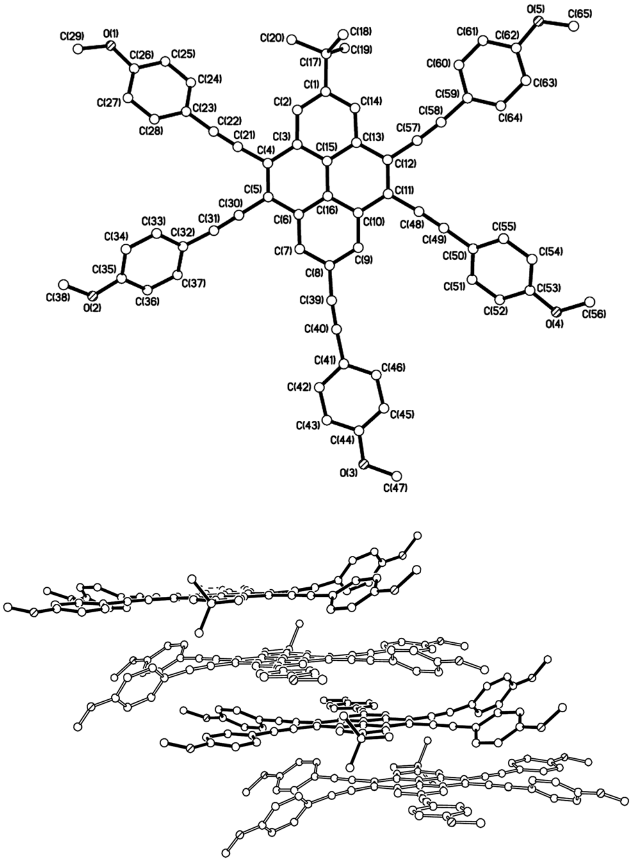

Fig. 1 X-ray structure diagrams of compound **4c**: (above) top view; (below) side view of 1-D slipped four molecules.

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lost the vibronic features compared to the corresponding spectra in solution. These hypsochromic shifts going from solution to the thin neat films are probably due to both the presence of strong intermolecular π–π aggregations and different molecular conformations.

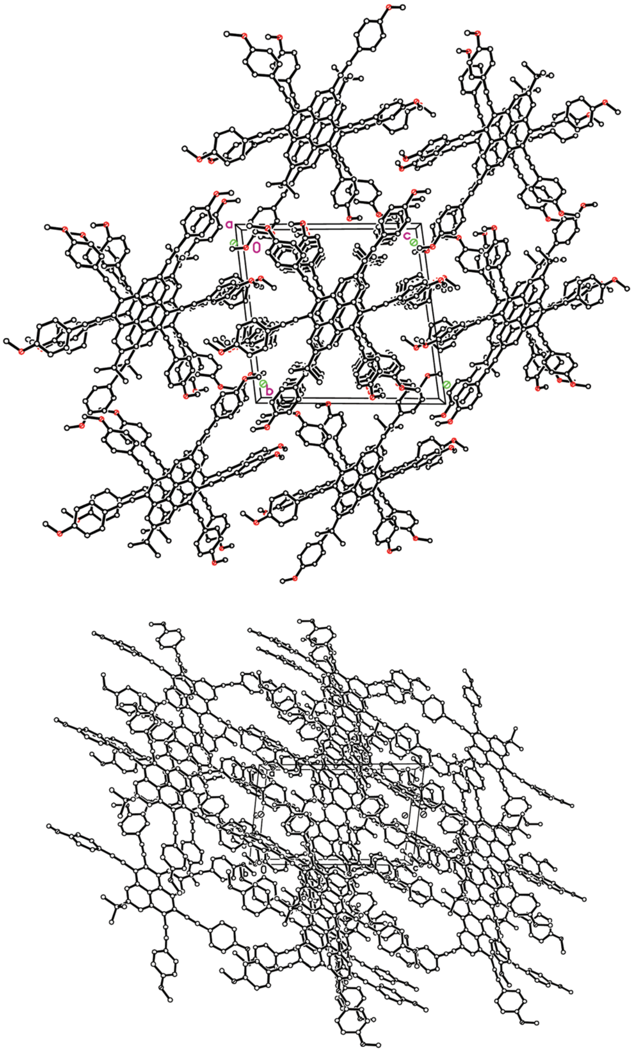

Fig. 2 Packing diagrams of compound **4c**: (above) view parallel to *a* highlighting π–π stacking; (below) view parallel to *b* showing herring-bone packing motif.

We investigated the electrochemical characteristics of the pyrenes **4** and **6** by using cyclic voltammetry (CV). The pyrenes were scanned both positively and negatively, separately, in 0.10 M tetrabutylammonium perchlorate (Bu_4NClO_4) in anhydrous dichloromethane with a scan rate of 50 mV s^{-1} at room temperature. We find that the oxidation and reduction of the pyrenes were quasi-reversible or reversible processes (see the ESI†). The onset potentials for oxidation were 0.86, 0.65, 0.62, and 1.42 V (*vs* SCE) for **4a**, **4b**, **4c**, and **6**, respectively. The onset potentials for reduction were −1.68, −1.47, −1.48, and −1.98 V (*vs* SCE), respectively. From the onset potentials of the oxidation and reduction processes, the band gaps (E_g) of the pyrenes were

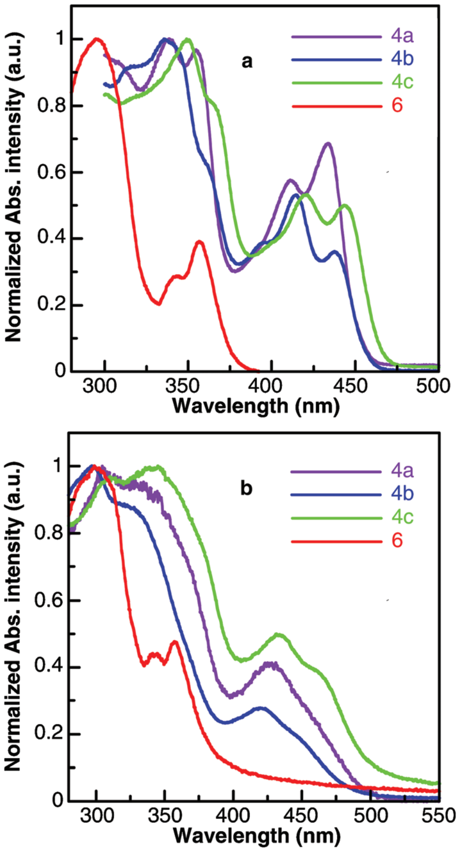

Fig. 3 Normalised UV/Vis absorption spectra of **4** and **6** recorded in CH_2Cl_2 (a) and in thin neat films (b).

Table 2 Photophysical and electrochemical properties of hand-shaped molecules **4** and **6**

Hand-shaped molecules	λ_{max} abs (nm)		λ_{max} PL (nm)		Φ_f^c solns/thin neat films/doped films	E_g^d (eV)	HOMO[e] (eV)	LUMO[f] (eV)	T_m^g (°C)	T_d^h (°C)
	solns[a]	films[b]	solns[a]	films[b]						
4a	433	428	454	558	0.46/0.12/0.38	2.54	−5.26	−2.72	326	507
4b	438	425	456	546	0.72/0.32/0.56	2.12	−5.05	−2.93	383	457
4c	443	431	463	553	0.86/0.16/0.45	2.10	−5.02	−2.92	315	453
6	355	357	411	414	0.24/0.17/0.15	3.40	−5.82	−2.42	nd	433

[a] Measured in dichloromethane at room temperature. [b] Measured in thin neat film. [c] Measured in dichloromethane, in neat thin film and 1 wt% doped polymethylmethacrylate (PMMA) films, respectively. [d] Determined from the LUMO and HOMO energy levels. [e] Calculated from the oxidation potentials. [f] Calculated from the reduction potentials. [g] Melting temperature (T_m) obtained from differential scanning calorimetry (DSC) measurement. [h] Decomposition temperature (T_d) obtained from thermogravimetric analysis (TGA).

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2.54, 2.12, 2.10, and 3.40 eV for **4a**, **4b**, **4c**, and **6**. Thus, according to the equations,[21,22] IP = − ($[E_{onset}]^{ox}$ + 4.4) eV and EA = − ($[E_{onset}]^{red}$ + 4.4) eV, where $[E_{onset}]^{ox}$ and $[E_{onset}]^{red}$ are the onset potentials for the oxidation and reduction of the pyrenes *versus* the reference electrode. The lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of the pyrenes were LUMO: −2.72, −2.93, −2.92, −2.42; HOMO: −5.26, −5.05, −5.02, and −5.82 eV for **4a**, **4b**, **4c**, and **6**, respectively. It was observed that the E_g values of **4a–4c** varied slightly due to the difference of the *p*-R-substituents, and indicates that different substituents in these pyrenes can inevitably result in different energy states of the whole molecule. Moreover, the calculated HOMO values of **4a–c** vary slightly in the range −5.26 to −5.02 eV, indicating that the materials are suitable for application in OLED-like optoelectronic devices.[18c] All data of electrochemical properties for the pyrenes **4** and **6** are summarized in Table 2.

The normalized PL emission spectra of the pyrenes **4** and **6**, upon excitation at the corresponding wavelength, both in CH_2Cl_2 solutions and in the thin neat films are shown in Fig. 4. For the non-conjugated pyrenes **6**, a deep-blue emission was observed with a long wavelength emission maximum at 411 nm and a shoulder band at *ca.* 430 nm in solution. However, for the alkynylpyrenes **4**, all emission spectra are largely bathochromically red-shifted into the sky-blue visible region; **4a**, **4b**, and **4c** showed a main emission at 454, 456, and 463 nm with a shoulder peak at 481, 484, and 488 nm, respectively. The emission difference between **4** and **6** should be ascribed to the ethynylene linkages that elongate the conjugation length of the molecules and make the molecules more planar with expanded π-delocalization. In addition, the emission spectra of the alkynylpyrenes **4** systematically varied in agreement with the electronic absorption spectra, implying that the energy gap between ground and excited states decreases in the order of **4a** > **4b** > **4c** (Table 2). The emission spectra are independent of the excitation wavelength. We further examined the effects of concentration on the fluorescence emission of **4c** in $CHCl_3$. Upon increasing the concentrations from 1.0×10^{-8} M to 1.0×10^{-4} M, we observed the intensities of the emission bands gradually increase, and the emissions correspond to only the monomer emission at 463 nm with shoulders at 444 and 488 nm (see ESI†). This result indicates that the presence of the single, sterically bulky, *t*Bu group at the 2-position can prevent two molecules of **4c** from getting close enough to result in excimer emission even at high concentrations.[12b]

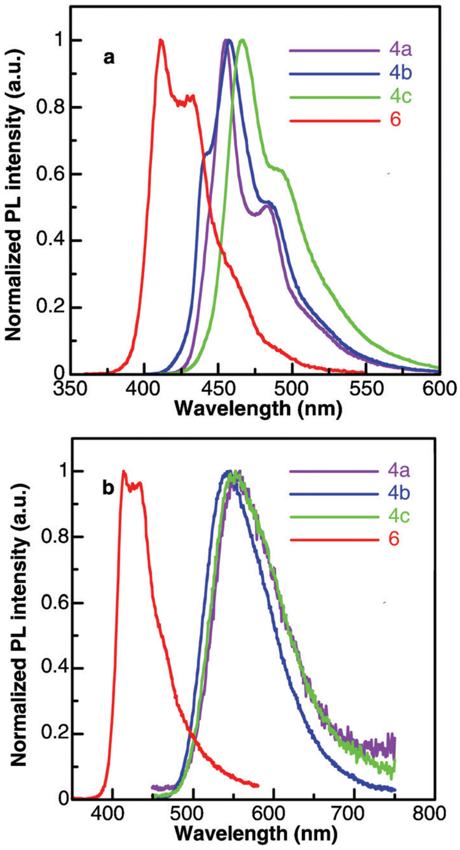

Fig. 4 Normalised fluorescence emission spectra of **4** and **6** recorded in CH_2Cl_2 (**a**) and in thin neat films (**b**).

In the thin neat films, the emission peak of the pyrene **6** shows a slight red-shift by *ca.* 3 nm, located at 414 nm, which points to only a marginal difference compared with that in solution. However, the main emission peaks of the alkynylpyrenes **4a**, **4b**, and **4c** were located at 558, 546, and 553 nm, respectively, with the disappearance of the fine structures of the spectra. The emissions are largely red-shifted by *ca.* 100 nm compared to those in solution. These large red-shifts of **4** in the thin neat films are probably due to the facile formation of strong intermolecular π–π aggregations between pyrene units[23] and the difference in dielectric constants of the environment,[24] which caused the low-energy emissions. The results are also consistent with the synchrotron single-crystal X-ray structure determination of the representative compound **4c**.

The fluorescence quantum yields of the pyrenes **4** and **6** recorded both in dilute CH_2Cl_2 solution and in the thin neat films at room temperature are also summarized in Table 2. For **6**, low quantum yields were obtained in solution and the thin neat films, which indicates that excitons were not confined to the whole backbone of **6** due to its non-conjugated molecular structure. Some energy loss might happen during the exciton migration,[25] thereby resulting in low quantum yields. Interestingly, for the hand-shaped alkynylpyrenes **4**, high fluorescence quantum yields were found in the range of 0.46–0.86 in solution, indicating the excitons were completely confined to the whole backbone of **4**, arising from the significantly expanded π-delocalization between the phenylacetylenic groups and the central pyrene core, thereby giving higher quantum yields. However, in the case of the thin neat films, the lower fluorescence quantum yields might be due to the facile formation of intermolecular π–π aggregations between pyrene units. Therefore, we further examined the photoluminescence (PL) spectra and the fluorescence quantum yields of **4** and **6** in thin films doped into polymethylmethacrylate (PMMA) at the 1 wt% level.[26] We observed a blue emission with a maximum peak at 448, 454, and 463 nm for **4a**, **4b**, and **4c**, respectively, which is similar to the corresponding emission in dilute solution (see ESI†). On the other hand, for the alkynylpyrenes **4**, higher quantum yields in the range 0.38–0.56 were observed in the 1 wt%-doped PMMA films, compared to the corresponding thin neat films, indicating the formation of strong intermolecular π–π aggregations of pyrene units can be

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avoided in the doped films. This result suggests the new alkynylpyrenes **4** might be promising dopants in the fabrication of host–guest-based organic light-emitting devices.[27] The quantum yields obtained for the pyrenes **4** are respectably high, which make them good candidates further investigations in optoelectronics with improved properties. All data are presented in Table 2.

Conclusions

In conclusion, we have developed three new alkynyl-functionalised, hand-shaped, π-conjugated emitters *via* the Sonogashira cross-coupling reaction in good yields and fully characterised the special chemical structures. The results obtained through inspecting the photophysical properties indicate that the extension of π-conjugation for these pyrene chromophores through phenylacetylenic substituents serves to shift the wavelength of absorption and fluorescence emission into the blue visible region with high fluorescence quantum yields. Synchrotron single-crystal X-ray analysis revealed that the single bulky *t*Bu group in the pyrene ring at the 2-position played a significant role in the molecular organization of the π stacking of the pyrene units. Thus, the herein presented molecules are exciting new materials that combine excellent optical features and improved thermal stabilities, which make them potential candidates in optoelectronic applications such as OLED-like devices, or models to investigate the fluorescent structure–property relationship of alkynylpyrenes. Further explorations into this area are ongoing.

Experimental

General

All the palladium-mediated cross-coupling reactions were performed under an argon gas atmosphere in oven-dried pressure tubes. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. The ^{1}H and ^{13}C NMR spectra were recorded on JEOL 300 (300 MHz and 75 MHz) spectrometers. The IR spectra were obtained as KBr pellets on a Nippon Denshi JIR-AQ2OM spectrometer. Mass spectra were obtained on a Nippon Denshi JMS-HX110A Ultrahigh Performance Mass Spectrometer at 75 eV using a direct-inlet system. Elemental analyses were performed with a Yanaco MT-5 analyser. Thermogravimetric analysis (TGA) was undertaken using a SEIKO EXSTAR 6000 TG/DTA 6200 unit under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. Differential scanning calorimetery (DSC) was performed using a Perkin–Elmer Diamond DSC Pyris instrument under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. UV-Vis spectra were measured using a Shimadzu UV-3150 UV-vis-NIR spectrophotometer. Photoluminescence spectra were obtained using a FluroMax-2 (Jobin-Yvon-Spex) luminescence spectrometer. Electrochemical properties of HOMO and LUMO energy levels were determined by Electrochemical Analyzer.

Materials

The preparations of 2,7-di-*tert*-butylpyrene and 4,5,9,10-tetrabromopyrene (**1**) were previously described.[13]

Lewis acid-catalysed *ipso*-bromination of 2,7-di-*tert*-butyl-4,5,9,10-tetrabromopyrene (1). To a mixture of 2,7-di-*tert*-butylpyrene (500 mg, 1.59 mmol), dry CH_2Cl_2 (250 mL) and 250 mg iron powder, a solution of Br_2 (1.0 g, 8.70 mmol) and CH_2Cl_2 (25 mL) was added drop wise over 1 h at 0 °C with stirring. After this addition, the mixture was warmed to room temperature and stirred for 8 h. Then, the mixture was poured into a large amount of ice water. The organic layer was washed successively with 10% aq. sodium thiosulfate (50 mL) and water (100 mL × 3), brine, dried (Na_2SO_4), and concentrated. The residue was washed with hot hexane (100 mL) and filtered to remove the byproducts. Then, the precipitate was washed with CH_2Cl_2 (50 mL) to give the desired compound **2** as a light-yellow solid (886 mg, 85%). M.p. 261 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.64$ (s, 9 H, *t*Bu), 8.87 (s, 2 H, Py-$H_{6,8}$), 8.90 (s, 2 H s, 2 H, Py-$H_{1,3}$) ppm. MS (EI): *m*/*z* 651.75 $[M]^+$. $C_{20}H_{13}Br_5$ (652.84): calcd. C 36.80, H 2.01; found C 37.06, H 2.12.

General procedure for the Sonogashira cross-coupling reaction towards the synthesis of 4. 4,5,7,9,10-Pentabromopyrene **2** (0.46 mmol), $[PdCl_2(PPh_3)_2]$ (0.023 mmol), CuI (0.023 mmol), PPh_3 (0.046 mmol) and the phenylacetylenes **3** (4.60 mmol) were added to a degassed solution of DMF (20 mL) and triethylamine (20 mL) under argon. The resulting mixture was stirred at 100 °C for the time mentioned in the individual cases. The reaction mixture was then cooled to room temperature and quenched with Et_2O and extracted. Solvent was removed to give the crude reaction mixture, which was further worked up as indicated in the individual cases.

Synthesis of 2-*tert*-butyl-4,5,7,9,10-*pentakis*-phenylethynylpyrene (4a). To a stirred mixture of 4,5,7,9,10-pentabromopyrene (300 mg, 0.46 mmol), Et_3N (20 mL) and DMF (20 mL), was added $PdCl_2(PPh_3)_2$ (17.3 mg, 0.023 mmol), CuI (4.6 mg, 0.023 mmol) and PPh_3 (11.80 mg, 0.046 mmol) stirring for 30 min at 0 °C under argon. Then, phenylacetylene (467 mg, 4.6 mmol) was added, the mixture was heated to 100 °C with stirring for 24 h. After cooling, the mixture was diluted into CH_2Cl_2 (200 mL) and washed successively with saturated NH_4Cl solution, H_2O and brine. The organics were dried ($MgSO_4$) and evaporated. The crude product was washed with ethyl acetate (150 mL) and separated by filtration. The filtrate was completely dissolved in CH_2Cl_2 and purified by column chromatography, eluting with hexane : CH_2Cl_2 (5 : 1) and recrystallization from toluene in hexane gave the desired product as a red-orange solid (168 mg, 48%); m.p. 326 °C. IR (KBr): 2955, 2198 (–C≡C–), 1655, 1510, 1268, 1018, 880, 835, 772, 656 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.68$ (s, 9 H, *t*Bu), 7.36–7.44 (m, 15 H, Ph), 7.63–7.82 (m, 10 H, Ph), 8.78 (s, 2 H, Py-$H_{1,3}$), 8.85 (s, 2 H, Py-$H_{6,8}$). ^{13}C NMR of this could not be determined due to its low solubility. MS (EI): *m*/*z* 758.36 $[M]^+$. $C_{60}H_{38}$ (758.94): calcd. C 94.95, H 5.05; found C 94.88, H 5.12.

Synthesis of 2-*tert*-butyl-4,5,7,9,10-*pentakis*(4-*tert*-butylphenyl ethynyl)pyrene (4b). To a stirred mixture of 4,5,7,9,10-pentabromopyrene (300 mg, 0.46 mmol), Et_3N (20 mL) and DMF (20 mL), was added $PdCl_2(PPh_3)_2$ (17.3 mg, 0.023 mmol), CuI (4.6 mg, 0.023 mmol) and PPh_3 (11.80 mg, 0.046 mmol) stirring

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for 30 min. at 0 °C under argon. Then, 4-*tert*-butylphenylacetylene (726 mg, 4.60 mmol) was added and the mixture was heated to 100 °C with stirring for 48 h. After cooling, the mixture was diluted with Et_2O (150 mL) and washed successively with saturated NH_4Cl solution (100 mL), H_2O and brine. The organics were dried ($MgSO_4$) and evaporated. The crude products were purified by column chromatography eluting with hexane and recrystallization from hexane gave the desired product as a yellow solid (200 mg, 42%); m.p. 383 °C. IR (KBr): ν = 2956, 2199 (–C≡C–), 1652, 1504, 1267, 1016, 879, 833, 761, 559 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.32 (s, 9 H, *t*Bu), 1.39 (s, 36 H, *t*Bu), 1.68 (s, 9 H, *t*Bu), 7.40–7.51 (m, 10 H, Ph), 7.63–7.78 (m, 10 H, Ph), 8.86 (s, 2 H, Py-$H_{1,3}$), 8.90 (s, 2 H, Py-$H_{6,8}$) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 31.3, 31.9, 34.8, 34.9, 35.6, 87.1, 87.2, 87.6, 89.1, 100.5, 100.7, 120.5, 120.6, 120.7, 120.8, 125.3, 125.4, 125.45, 125.47, 125,50, 125.52, 125.54, 129.7, 130.0, 130.1, 130.6, 131.7, 131.75, 131.83, 151.5, 151.7, 151.8, 151.9 ppm. MS (EI): *m*/*z* 1038.67 $[M]^+$. $C_{80}H_{78}$ (1039.48): calcd. C 92.44, H 7.56; found C 92.26, H 7.46.

Synthesis of 2-*tert*-butyl-4,5,7,9,10-*pentakis*(4-methoxyphenylethynyl)pyrene (4c). To a stirred mixture of 4,5,7,9,10-pentabromopyrene (300 mg, 0.46 mmol), Et_3N (20 mL) and DMF (20 mL), added $PdCl_2(PPh_3)_2$ (17.3 mg, 0.023 mmol), CuI (4.6 mg, 0.023 mmol) and PPh_3 (11.80 mg, 0.046 mmol) stirring for 30 min. at 0 °C under argon. Then, 4-ethynylanisole (611 mg, 4.6 mmol) was added, the mixture was heated to 100 °C and stirred for 48 h. After cooling, the mixture was diluted into CH_2Cl_2 (200 mL) and washed successively with saturated NH_4Cl solution (100 mL), H_2O and brine. The organic layer was dried ($MgSO_4$) and evaporated. The crude products were washed with ethyl acetate (45 mL) and purified by column chromatography eluting with hexane : CH_2Cl_2 6 : 1 and recrystallization from toluene in hexane gave the desired compound as a yellow solid (192 mg, 46%); m.p. 315 °C. IR (KBr): ν = 2958, 2195 (–C═C–), 1762, 1610, 1512, 1255, 1176, 1031, 831, 537 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ = 1.68 (s, 9 H, *t*Bu), 3.88 (s, 3 H, *OMe*), 3.89 (s, 12 H, *OMe*), 6.94–6.99 (m, 10 H, Ph), 7.63–7.76 (m, 10 H, Ph), 8.86 (s, 2 H, Py-$H_{1,3}$), 8.89 (s, 2 H, Py-$H_{6,8}$) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 31.9, 35.7, 55.4, 86.6, 86.8, 89.3, 90.5, 99.7, 100.2, 114.2, 114.3, 114.4, 115.9, 116.1, 120.8, 121.9, 123.0, 123.1, 123.3, 124.9, 128.1, 129.8, 130.0, 133.3, 133.4, 133.5, 150.3, 159.9, 160.0, 160.1, 160.2 ppm. MS (EI): *m*/*z* 908.34 $[M]^+$. $C_{65}H_{48}O_5$ (909.07): calcd. C 85.88, H 5.32; found C 85.82, H 5.26.

Synthesis of 2-*tert*-butyl-4,5,7,9,10-*pentakis*(4-methoxyphenyl)pyrene (6).[14] To a mixture of 2,4,5,9,10-tetrabromo-7-*tert*-butylpyrene (300 mg, 0.46 mmol), 4-methoxyphenylboronic acid **5** (561 mg, 4.60 mmol) in toluene (80 mL) and ethanol (40 mL) at room temperature with stirring under argon, was added Na_2CO_3 (2 M, 20 mL) solution and $Pd(PPh_3)_4$ (110 mg, 0.096 mmol). The mixture was heated to 70 °C stirring over night. After cooling to room temperature, the mixture was quenched with water, extracted with CH_2Cl_2 (500 mL), and washed with water and then brine. The organic extracts were dried with $MgSO_4$ and evaporated. The residue was firstly washed with ethyl acetate (10 mL) and then purified by column chromatography eluting with hexane to give **6** as a white solid (105 mg, 36%); ^1H NMR (300 MHz, $CDCl_3$): δ = 1.26 (s, 9 H, *t*Bu), 3.81 (s, 3 H, *OMe*), 3.83 (s, 6 H, *OMe*), 3.84 (s, 6 H, *OMe*), 6.86 (d, *J* = 8.79 Hz, 4 H, Ph), 6.87 (d, *J* = 8.79 Hz, 4 H, Ph), 6.92 (d, *J* = 8.79 Hz, 2 H, Ph), 7.20 (d, *J* = 8.61 Hz, 4 H, Ph), 7.21 (d, *J* = 8.58 Hz, 4 H, Ph), 7.45 (d, *J* = 8.79 Hz, 2 H, Ph), 7.93 (s, 2 H, Py-$H_{1,3}$), 8.02 (s, 2 H, Py-$H_{6,8}$) ppm.^{13}C NMR (300 MHz, $CDCl_3$): δ = 31.7, 35.4, 55.2, 55.4, 113.2, 113.3, 113.5, 114.3, 122.0, 122.3, 122.8, 123.0, 128.9, 129.0, 131.0, 131.4, 132.0, 132.2, 132.3, 134.6, 137.7, 137.8, 138.3, 148.5, 158.0, 159.1 ppm. MS (EI): *m*/*z* 789.82 $[M]^+$. $C_{55}H_{48}O_5$ (789.97): calcd. C 83.73, H 6.13; found C 83.62, H 6.15.

Crystal data and refinement details for 4c

Diffraction data were collected at the Advanced Light Source (ALS) Station 11.3.1 using a Bruker SMART APEX II CCD diffractometer using narrow frames to θ_{max} = 26.46°.[28] Data were corrected for absorption on the basis of symmetry equivalence and repeated data (min. and max. transmission factors: 0.975, 0.998) and Lp effects. The structure was solved by direct methods and refined on F^2 using all data.[29] H atoms were constrained in a riding model. Over a centre of symmetry, two residual peaks, with a separation consistent with that of the two chlorine atoms in dichloromethane, were successfully modelled as a small amount of CH_2Cl_2 of crystallisation. Further details can be found in Table 1 and ref. 15

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