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COMMUNICATION

Core-extended rylene dyes via thiophene annulation[†]‡

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Annulation of thiophenes directly into the bay regions of rylene dyes through effective Stille coupling and subsequent ring-fusion under Scholl conditions leads to core-extended rylene tetracarboxylic diimides with interesting electro-optical properties.

Rylene dyes are based on naphthalene units linked at the periposition. The most important representatives are perylene-3,4:9,10-tetracarboxylic acid diimides (PDIs, n = 2, Fig. 1). Due to their remarkable electro-optical properties, PDIs have received a great deal of attention as promising organic n-type semiconducting materials which have found widespread applications.¹ Chemical modifications both at the imide groups and in the pervlene core are two different successful synthetic strategies for a diverse library of perylene diimides.² However, the dramatic change of optical and electronic properties can only be achieved by the bay-functionalization because of nodes in the HOMO and LUMO orbitals at the imide nitrogen atoms. While the effective synthesis of terrylene- (TDIs, n = 3, Fig. 1) and quaterrylene tetracarboxylic diimides (ODIs, n = 4, Fig. 1) was described in the last decade,³ modifications in the bay region to achieve extension of the conjugation are rarely reported.⁴

Significant progress has been achieved in the development of high performance organic semiconductors based on thiophene and its derivatives due to their synthetic availability, widespread possibility, and tunable electronic properties.⁵ We are particularly interested in the bay-region functionalization of rylene dyes and hetero-atom decorated organic semiconductors.⁶ In previous



Fig. 1 Rylene dyes (n = 1, 2, 3, 4) and S-annulated PDI.

work, we report the facile synthesis of a novel PDI that is *S*-heterocyclic annulated in two bay-regions (SPDI, **2**, Fig. 1).⁷ The palladium-catalyzed reaction of bis(tributylstannyl) sulfide with aryl chloride easily converts an extremely twisted precursor molecule to a planar product. Herein, we present a new synthetic approach combining the palladium-catalyzed Stille cross-coupling of halogenated rylene dyes with 2-(tributylstannyl) thiophene and subsequent ring-fusion under Scholl conditions, which lead to a series of thiophene-annulated core-extended rylene dyes with interesting electro-optical properties.

The synthesis of thiophene-annulated rylene dyes is outlined in Scheme 1. As reported by Würthner et al., the regioisomerically pure 1,7-dibromo PDI is prepared by repetitive recrystallization from a mixture of 1,6- and 1,7-dibromo PDIs.8 Tetrabromo-TDI and hexabromo-ODI are prepared by using the procedures reported in ref. 9. Although the aryloxylated TDIs and QDIs can be facilely prepared by simple aryloxylation of halogenated rylene dyes,¹⁰ the transition-metal catalyzed cross-coupling reaction of halogenated TDIs and QDIs is rarely investigated. Stille cross-coupling of halogenated rylene dyes with 2-(tributylstannyl)thiophene proceeds smoothly to introduce thiophene units directly into the bay regions of TDI in good yields. It is remarkable that the regioisomerically pure 1,6,8,11,16,18hexa-thiopheneyl substituted QDI could be separated from it's isomer 1,6,9,11,16,18-hexa-thiopheneyl substituted QDI (less quantity) in moderate yields, while the hexa-brominated QDIs contain unseparated mixtures of isomers.

Remarkably, when brominated PDIs are treated with 2-(tributylstannyl)thiophene under the standard Stille conditions, they directly afford the desired heterocyclic annulated PDIs in a yield of 75%. As reported quite recently for pyridyl substituted PDIs,¹¹ the thiopheneyl substituted PDIs are also highly inclined to cyclization probably promoted by visible light.

Differing from the thiopheneyl substituted PDIs, the thiopheneyl substituted TDIs (6) and QDIs (7) are obtained in 73% and 36% yield respectively. Following the critical final cyclodehydrogenation step under Scholl conditions using ferric chloride, the desired thiopheneyl annulated TDI (9) and QDI (10) are achieved in high yields. It should be noted that oxidative cyclodehydrogenation with ferric chloride is sometimes limited by the electronic character of the substituents.¹² Typically, phenyl rings bearing electron-withdrawing groups are less active in the cyclodehydrogenation reaction. Thus, the successful cyclodehydrogenation of 6 and 7 to afford the desired product is particularly significant.

In order to gain insight into the structure of molecules **8**, **9** and **10**, B3LYP/6-31G* calculations were carried out. The optimized

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Scheme 1 Synthesis of the regiospecifically thiophene-annulated rylenes: (i) 2-(tributylstannyl)thiophene, Pd(PPh₃)₄, toluene, 110 $^{\circ}$ C, 24 h. Yields: 75% for 8; 73% for 6; 36% for 7. (ii) FeCl₃, dichloromethane, room temperature. Yields: 92% for 9; 90% for 10.

structures are shown in Fig. S2 (ESI[‡]). Owing to the steric encumbrance effect between thiophene rings and neighbouring hydrogens, optimized geometries of 9 and 10 are markedly non-planar while the extended conjugated core in 8 is fully planar. Similarly to PDI derivatives featuring large substituents in the bay region, the twisted core in the lowest energy conformers of 9 and 10 is associated with thiophenic substituents in *anti*.

Room-temperature absorption and emission spectra of these compounds are shown in Fig. 2 and Fig. S6 (ESI‡), where a comparison with TD-B3LYP/6-31G* spectra, computed at the optimized geometries, are also reported. Both **6** and **7** display broad absorption peaks with a maximum at 738 nm and 876 nm (see Fig. S6, ESI‡), bathochromically shifted by 88 nm and 116 nm compared with parent terrylene diimides and quaterrylene diimides,^{3b,c} respectively. Inspection of the computed lowest-energy electronic transition of **6** and **7** reveals that it is dominated by the HOMO \rightarrow LUMO excitation, with frontier orbitals conserving the rylene diimide character. The observed bathochromic shift is therefore ascribed to the electron



Fig. 2 Comparison between TD-B3LYP/6-31G* computed (bottom) and observed (top) UV/vis absorption spectra of 8 (black line), 9 (green line) and 10 (red line) in CHCl₃ (1×10^{-5} M) at room temperature. Inset: emission spectra of 8 (black line), 9 (green line) and 10 (red line).

rich character of the thiophene substituents that results in higher energy HOMO orbitals of **6** and **7** compared to their parent rylene diimides (Fig. S7, ESI \ddagger). Finally, the broadening is attributed to the rotational flexibility of thiophene substituents and to the availability of a number of low energy conformational isomers of **6** and **7**.

Thiopheneyl annulated rylenes 8, 9 and 10 show a limited solubility in common organic solvents. The orange solution of 8 shows three major bands at 360, 472, 524 nm ($\varepsilon_{\lambda_{max}}$ $25\,310 \text{ M}^{-1} \text{ cm}^{-1}$) with a slight hypsochromic shift relative to parent PDI (N,N'-di(2,6-diisopropylphenyl) perylene-3,4:9,10tetracarboxylic acid diimide), the shape of which is in contrast to that of dibenzo- and dipyrido-coronene diimides.96,11 Inspection of the computed lowest energy transitions of 8 reveals, however, a close parentage with those of unsubstituted coronene diimide CDI.^{11b} The more extended conjugation driven by the thiophene moieties, coupled with their electron rich character, pushes the HOMO and HOMO - 1 levels of 8 to higher energies such that the electronic transitions to the two lowest energy singlet excited states of 8 are bathochromically shifted compared to those of CDI (see Fig. S9, ESI[‡]). The red solution of 9 and olive solution of 10 exhibit also three major bands at 418, 530, 600 nm $(\epsilon_{\lambda_{max}}$ = 17872 $M^{-1}~cm^{-1}),$ and 454, 568, 634 nm $(\epsilon_{\lambda_{max}}$ = $27\,296$ M⁻¹ cm⁻¹) bathochromically shifted 76 nm and 110 nm in comparison with 8, respectively, as a reflection of largely extensive conjugation over the π -electronic system.

It should be also noted after the annulation that **9** and **10** are hypsochromically-shifted relative to the corresponding parent

Table 1 Electro-optical properties of thiophene-annulated rylene dyes

	λ_{abs}/nm	$\lambda_{\rm em}/{\rm nm}$	$E_{\rm red}^{1\ a}/{ m V}$	$E_{\rm red}^2{}^a/{ m V}$	$E_{\mathrm{ox}}^{1\ b}/\mathrm{V}$	$E_{\mathrm{ox}}^{2\ b}/\mathrm{V}$	$E_{\rm g}{}^c/{ m eV}$
8 9 10	524 600 634	532 612 644	-0.78 -0.87 $\{d}$	$-1.00 \\ -1.00 \\ _^d$	 1.37 1.19	 1.46	2.30 2.00 1.88

^{*a*} Half-wave reductive potential (in V *vs.* Ag/AgCl) measured in CH₂Cl₂ at a scan rate of 0.1 V s⁻¹ with ferrocene as an internal potential marker. ^{*b*} Half-wave oxidative potential (in V *vs.* Ag/AgCl) measured in CH₂Cl₂ at a scan rate of 0.1 V s⁻¹. ^{*c*} Obtained from the edge of the absorption spectra. ^{*d*} The CVs of compound **10** did not provide well-defined reduction peaks probably because of poor solubility.

TDIs and QDIs (50 nm for **9** and 126 nm for **10** respectively) as a reflection of the extended rylene core along the short molecular axis. Meanwhile, thiopheneyl annulated rylenes **8**, **9** and **10** possess small Stokes shifts (8–12 nm) and high fluorescence quantum yields (0.56 for **9** and 0.14 for **10** using cresyl violet as a standard, and around 1 for **8** using parent PDI as a standard, see ESI‡), which means that the introduction of thiophene units into the bay region of rylenes could effectively modulate the absorption in keeping high fluorescence quantum yields.

The electrochemical properties of thiopheneyl annulated rylenes are also investigated by cyclic voltammetry in dichloromethane (vs. Ag/AgCl), and their reductive and oxidative potentials are given in Table 1. Cyclovoltammograms of 8, 9 and 10 are shown in Fig. S1 (ESI[‡]). The thiopheneyl annulated PDI 8 exhibits two reversible reduction waves, whereas within the accessible scanning range in dichloromethane no oxidation waves could be detected. The first reduction wave for 8 is observed at -0.78 V vs. Ag/AgCl, whereas the second reduction wave appeared at -1.00 V. In contrast to 8, thiopheneyl annulated TDI 9 shows two reversible reduction waves and one reversible oxidation wave, and thiopheneyl annulated QDI 10 has two reversible oxidation waves in the absence of well-defined reduction peaks probably because of poor solubility. The first reduction wave of 9 is at a slightly lower potential than that of 8, whereas the first oxidation wave of 10 is at a lower potential than that of 9, indicating that the introduction of thiopheneyl units into the bay region of rylene dyes makes them suitable electron donors and acceptors. This conclusion is strongly supported by the energy trend displayed by the frontier molecular orbitals of 8, 9 and 10 (see Fig. S10, ESI[‡]) and showing a modest energy change of the LUMO level and a remarkable energy increase of the occupied orbitals of 9 and 10.

In summary, we report a new synthetic approach combining the palladium-catalyzed Stille cross-coupling of halogenated rylene dyes with 2-(tributylstannyl) thiophene and subsequent ring-fusion under Scholl conditions. The introduction of thiopheneyl groups directly into the core has drastically influenced the optical and electronic properties of rylenes which shows a modest energy change of the LUMO level and a remarkable energy increase of the occupied orbitals. Further studies on functionalization of thiopheneyl annulated rylenes and their applications as ambipolar materials in electronic devices are currently underway.

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