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H-Shaped OPE/OPV Oligomers: A New Member of 2D-Conjugated Fluorophore Cores

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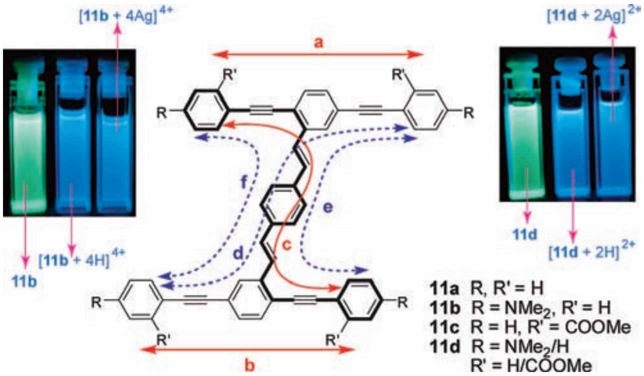
ABSTRACT



A new class of two-dimensional (2D), π-conjugated, skewed H-shaped co-oligomers of phenylene vinylene and phenylene ethynylene (11a−d, termed H-mers) were synthesized using Sonogashira coupling and Wittig−Horner reactions as the key steps. Electronic and spectroscopic properties of the H-mers were investigated by UV−vis absorption, fluorescence spectroscopic techniques, and ab initio calculations (HF/3-21G). Two amino-containing functional H-mers (11b and 11d) were found to exhibit appealing fluorescence sensitivity to selected Brønsted acids and transition-metal ions.

For decades, linear π-conjugated oligomers have been the mainstay of advanced molecular materials for new electronic and optoelectronic devices.[1] Higher order, multidimensional π-conjugated oligomeric systems, such as 2D arylene-based π-conjugated oligomers,[2] started to draw serious research attention only within the past few years. Recent representative contributions include cross-shaped oligo(phenylene ethynylenes) (OPEs),[3] oligo(phenylene vinylenes) (OPVs),[4] oligo(thiophenes) (OTs),[5] swivel cruciform OTs,[6] cruciform OPE/OPV co-oligomers,[7] and others. [8] The emergence of these new conjugated materials has greatly widened the scope of molecular candidates applicable in molecular sensors,[3a,7a–e] switches,[9] nonlinear

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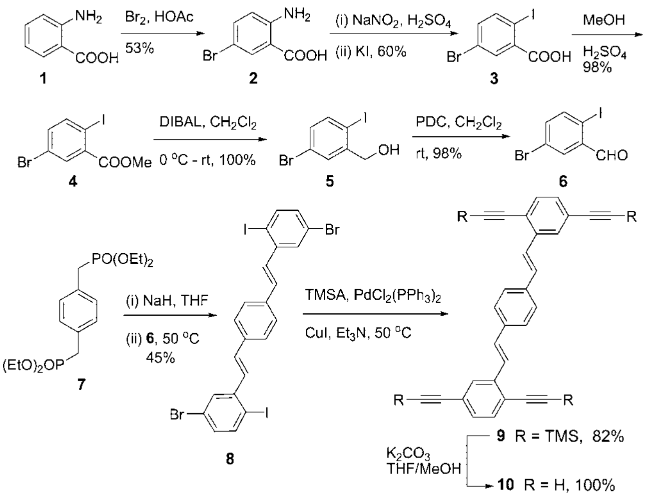
optical (NLO) materials,[10] organic field effect transistors (OFETs),[5] and photoluminescence.[3a]

In this contribution, a new class of skewed, H-shaped π-conjugated co-oligomers based on linear OPE and OPV fragments were synthesized and investigated. These oligomers, termed "H-mers" due to their unique H-shaped π-topology as illustrated in the graphical abstract, possess distinct π-electron delocalization patterns with three linear conjugation paths a, b and c, where path c (highlighted bold) represents the longest linear conjugation route. Paths d, e, and f, indicated by dashed lines, are cross-conjugated, along which weak electronic communications may be induced as well.[11] The design criteria of the H-mer structure were aimed to create a series of new 2D π-fluorophore cores whose electronic and photonic behavior can be flexibly manipulated or finely tuned by means of chemical functionalization with various electroactive and chromophoric groups.

Scheme 1. Synthesis of Tetraethynyl OPV Building Block **10**



Synthetic routes to an OPE/OPV H-mer **11a** and its donor/acceptor (D/A) functionalized derivatives **11b**−**d** have been successfully developed. In Scheme 1, the synthesis of a tetraethynylated OPV building block **10** essential for the construction of H-mers is described. The synthesis began with bromination of 2-aminobenzoic acid (**1**), leading to 2-amino-5-bromobenzoic acid (**2**). Compound **2** underwent diazotization followed by treatment with KI to afford 5-bromo-2-iodobenzoic acid (**3**), which was then subjected to a Fischer esterification with MeOH in the presence of H_2SO_4, yielding methyl ester **4**. Compound **4** was reduced into benzyl alchohol **5** by diisobutylaluminum hydride (DIBAL). Oxidation of **5** with pyridinium dichromate (PDC) resulted in 5-bromo-2-iodobenzaldehyde (**6**) in a high yield. Compound **6** underwent a Wittig−Horner reaction with the phosphonate ylide that was generated by treating **7** with NaH, affording dibromodiiodo-OPV percursor **8**. Sonogashira coupling of **8** with trimethylsilylacetylene (TMSA) under the catalysis of Pd/Cu gave compound **9**, which was further desilylated with K_2CO_3 to afford the desired tetraethynyl OPV **10** in an almost quantitative yield.

The facile preparation of **10** allowed the construction of symmetrically functionalized H-mers to be readily performed via a Sonogashira cross-coupling protocol. As shown in Scheme 2, a basic H-mer scaffold **11a**, a donor (D)-functionalized H-mer **11b**, and an acceptor (A)-functionalized H-mer **11c** could be obtained in decent yields through the cross-coupling reactions.

The synthesis of a D−A-substituted, electron "push−pull" H-mer **11d**, however, required a different strategy in which an unsymmetrically silyl-protected precursor **14a** was necessary. Compound **14a** was prepared via a sequence of Sonogashira coupling and Wittig−Horner reactions as outlined in Scheme 3. Selective removal of the TMS groups in **14a** with K_2CO_3 afforded bis-terminal alkyne **14b**, which was subjected to Sonogashira coupling with methyl 2-iodobenzoate to yield compound **15a**. Desilylation of **15a** with TBAF followed by Sonogashira coupling with 4-iodo-*N*,*N*-dimethylaniline employing $PdCl_2(PPh_3)_2$/CuI as catalyst and piperidine as base furnished D−A substituted H-mer **11d** in a satisfactory yield.

The electron-donating and -accepting groups appended to the phenyl termini of the H-mer backbone were anticipated to significantly modulate π-electronic characteristics.[12] The substitution effects on structures and electron density of the H-mers **11a-d**[13] were evaluated by ab initio calculations (HF/3-21G) using Spartan'06.[14] The computational results are quite revealing in terms of the sensitivity of FMOs to the electronic nature of the substituents; D and A functionalities are found to result in different energetics and distributions of FMOs (see Figure 1a and the Supporting Information). The calculated HOMO−LUMO gaps of four H-mers are **11a**

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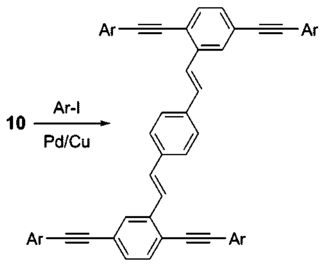
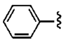
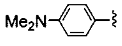
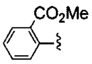
(13) The NMe_2 and COOMe groups of **11b**−**d** were replaced with NH_2 and COOH groups in the calculations to reduce computational expense. Details are given in the Supporting Information.

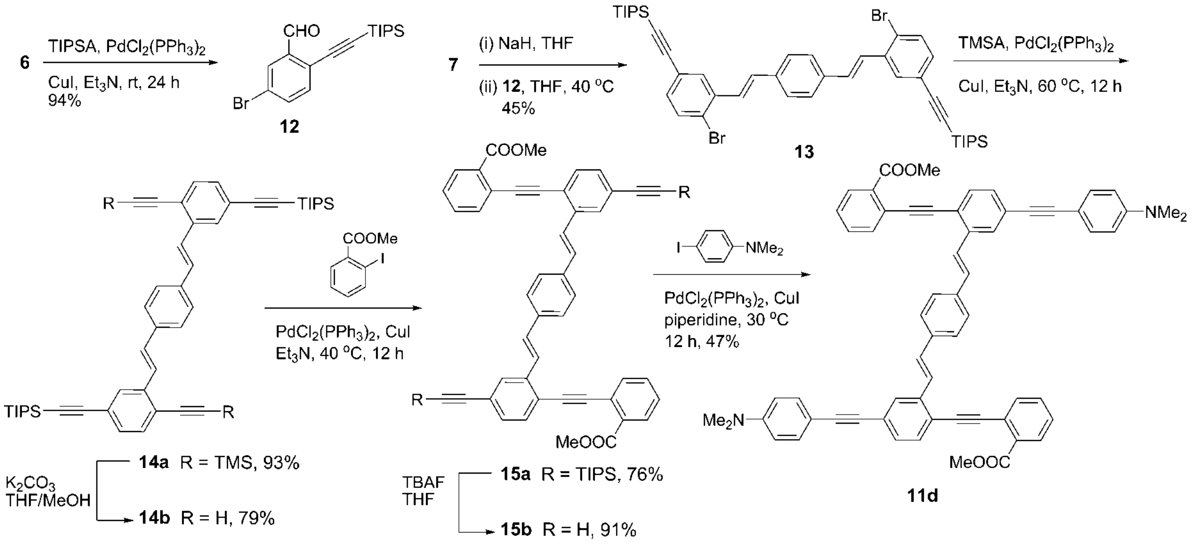
(14) Spartan'06 software, Wavefunction Inc., Irvine, CA.

Scheme 2. Synthesis and Symmetrically Functionalized H-mers



	Ar	catalyst/base	yield (%)
11a		$PdCl_2(PPh_3)_2$, CuI/ piperidine	67
11b		$PdCl_2(PPh_3)_2$, CuI/ Piperidine	79
11c		$PdCl_2(PPh_3)_2$, CuI/ Et_3N	70

Scheme 3. Synthesis of D-A Functionalized H-mer **11d**



(8.86 eV) > **11c** (8.58 eV) > **11d** (8.45 eV) > **11b** (8.27 eV). The order of decreasing HOMO−LUMO gaps is in good agreement with the trend of redshift of the maximum absorption wavelengths (λ_{max}) of the H-mers, which can be clearly observed in Figure 1b as **11a** (327 nm) < **11c** (345 nm) < **11d** (358 nm) < **11b** (367 nm).

The first excited-state (S_1) properties of H-mers **11a**−**d** were probed by steady-state fluorescence spectroscopy, and the detailed spectra are given in Figure 1c. The spectrum of unfunctionalized H-mer **11a** features a distinct vibronic progression with three bands at 425, 450, and 480(sh) nm. The vibronic spacing is 1348 cm^{-1}, which is attributed to an averaged vibrational mode, with the largest contribution from the C═C stretch in the central vinylene moiety.[15] The emissions from A-substituted H-mer **11c** are observed at 442, 462, 491(sh) nm, only slightly red-shifted relative to that of **11a**. For D−A-substituted H-mer **11d** and D-substituted H-mer **11b**, vibronic bands were not observed at room temperature, but a broad monotonous peak centered at 500 (**11d**) and 506 nm (**11b**).[16] Unlike **11c**, the maximum emission wavelengths (λ_{em}) of **11b** and **11d** are substantially red-shifted relative to **11a**. The trend of fluorescence spectral shift is consistent with the UV−vis data and ab initio calculations.

The ab initio calculations for **11b** and **11d**, both of which contain NMe_2 substituents, reveal that the electron density for FMOs undergoes a dramatic change when protonated (see the Suporting Information). If true, protonation or metal coordination to NMe_2 will give rise to significant change in the absorption/emission spectra, which can be exploited in molecular sensor devices.[7a−e] To shed more light on this aspect, trifluoroacetic acid (TFA) and AgOTf were selected as two testing substrates to be added into the solutions of **11b** and **11d** in chloroform. These titration processes were monitored by UV−vis and fluorescence spectroscopy as shown in Figure 1d−k.

For H-mer **11b**, addition of TFA caused a considerable attenuation of the absorption peak at 367 nm, and a new band at 329 nm was observed whose intensity increased with increasing [H^+] (Figure 1d). The emission intensity of **11b** at 506 nm under the same acid titration was considerably reduced, while three new bands at 431, 452, and 485(sh) nm emerged with increasing acidity. It is noted that both

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(16) The D-substituted H-mers **11b** and **11d** have ICT states that result in significantly increased reorganization energy and band broadening.

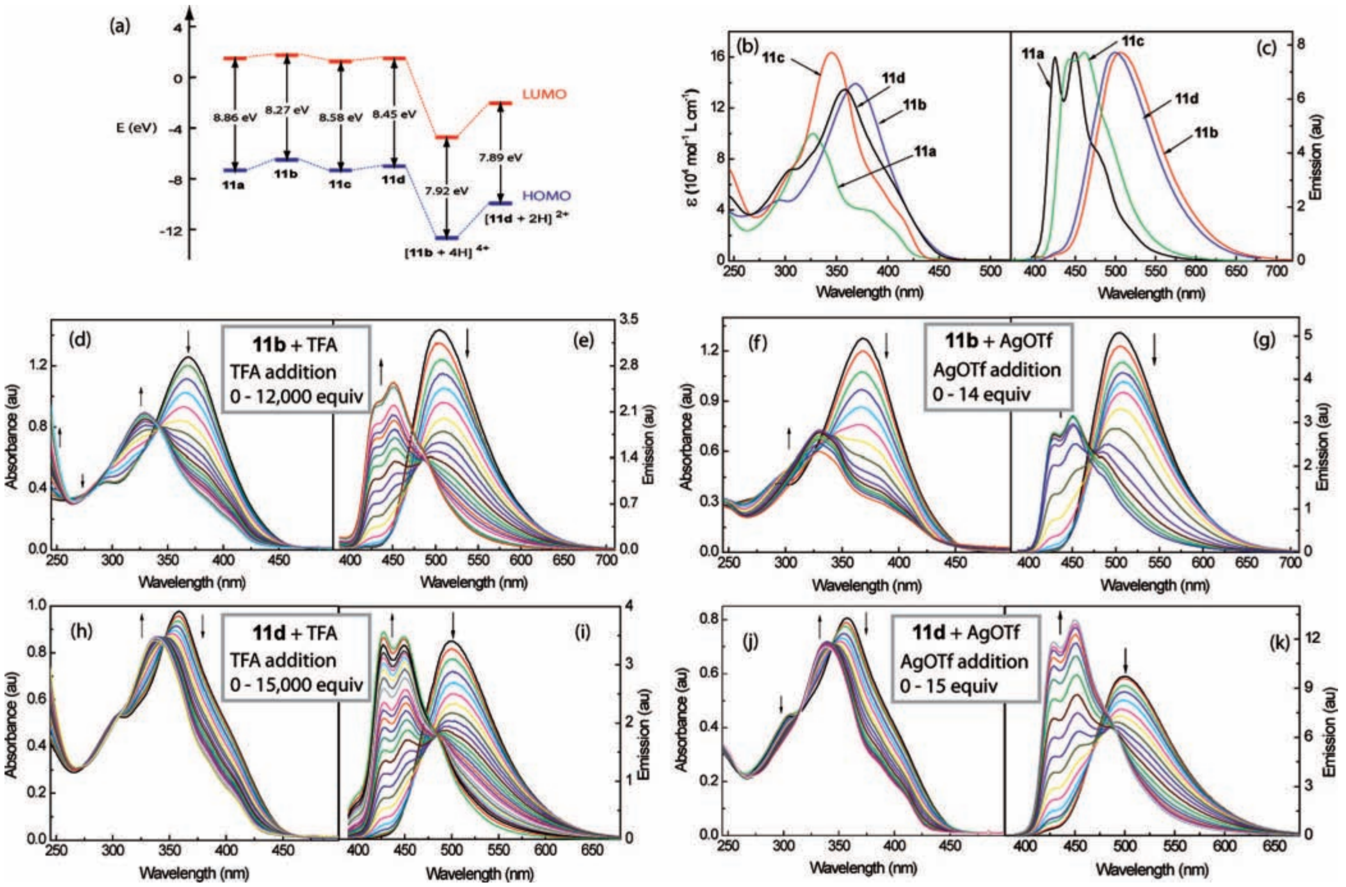

Figure 1. (a) Diagram of FMO energy levels. (b) UV−vis spectra of **11a**−**d**. (c) Fluorescence spectra of **11a**−**d**. Quantum yields (Φ): 49% (**11a**, $\lambda_{ex} = 326$ nm), 43% (**11b**, $\lambda_{ex} = 367$ nm), 36% (**11c**, $\lambda_{ex} = 345$ nm), and 56% (**11d**, $\lambda_{ex} = 358$ nm). (d) UV−vis and (e) fluorescence titrations of **11b** with TFA. (f) UV−vis and (g) fluorescence titrations of **11b** with AgOTf. (h) UV−vis and (i) fluorescence titrations of **11d** with TFA. (j) UV−vis and (k) fluorescence titrations of **11d** with AgOTf.

the UV−vis and fluorescence profiles of **11b** after exhaustive TFA protonation (saturation reached at ca. 12000 molar equiv of TFA) bear great resemblance to those of the unfunctionalized H-mer **11a**. This result indicates that protonation of **11b** significantly attenuated the ability of the NMe_2 to donate electrons, and the resulting ammonium groups in [**11b** + 4H]$^{4+}$, which can only exert an inductive withdrawing effect, have virtually no or little influence on the electronic features of the entire H-mer core. Titration of AgOTf to **11b** resulted in similar UV−vis and fluorescence spectral changes to those observed in TFA titration (see Figure 1f,g); however, saturation of titration was reached at only ca. 14 molar equiv of Ag^+ due to a substantial change in the binding constant (ΔG^o_b) increasing the equilibrium.

The spectral changes of **11d** in response to titration of TFA or AgOTf (Figure 1h−k) were similar to the titration behavior of **11b**. The UV−vis and fluorescence profiles of [**11d** + 2H]$^{2+}$ and [**11d** + 2Ag]$^{2+}$ are found to resemble those of A-substituted **11c** both in shape and λ_{max} value, indicating that the NMe_2 groups function as the active electron donors to interact with TFA or AgOTf. It is also notable that fluorescence intensity of **11d** after saturation with AgOTf became significantly higher.

In conclusion, the synthesis of D/A functionalized OPE/OPV H-mers has been successfully developed. Their FMO and related electronic spectral properties are tunable through electronic substitution effects. The spectral titration outcomes for **11b** and **11d** with TFA and AgOTf signify the fluorescence sensing function of these functionalized H-mers. Further exploration on the molecular sensory applications of functional H-mers is underway, and detailed results will be disclosed in due course.

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Supporting Information Available: Experimental procedures, synthetic and spectroscopic data for compounds **2**−**15**, and details of computational studies of **11a**−**d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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