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Multitiered 2D π-Stacked Conjugated Polymers Based on Pseudo-Geminal Disubstituted [2.2]Paracyclophane

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Abstract: Interchain interactions between π-systems have a strong effect on the electronic structure of conjugated organic materials. This influence has previously been explored by the spectroscopic and electrochemical characterization of molecules in which pairs of conjugated oligomers are held in a stacked fashion by attachment to a rigid scaffold. We have prepared a new polymer which uses a pseudo-geminal disubstituted [2.2]paracyclophane scaffold to hold 1,4-bis(phenylethynyl)-2,5-dialkoxybenzene (PE_3) chomophores in a π-stacked fashion over their entire length and in an extended multitier arrangement. Solutions of this new polymer display a Stokes shift of 171 nm, compared to just ca. 30 nm for previous models in which only the terminal phenyl rings of the PE_3 chromophore are held in a stacked arrangement. This suggests that interchain interactions of π-systems over their entire length in a multitier assembly provides for relaxation of the excited state to a stable "phane" electronic state which is responsible for emission. This stabilization is not available in the stacked dimer or other regioisomers of the polymer which possess lesser degrees of overlap. Thus, the architecture of the soluble polymer mimics that of segments of conjugated polymers in semiconducting thin films and will provide a platform for the exploration of the nature of charge carriers and excitons in these important materials.

Semiconducting conjugated oligomers and polymers have promise in a variety of applications by virtue of their unique combination of mechanical, electronic, and optical properties.[1] Interchain interactions between closely packed conjugated chains in the solid state exert a strong influence on the electronic structures of the materials: These have been investigated by both computational[2] and experimental methods.[3] Significant effort has been made to explore interactions between π-systems by the spectroscopic and electrochemical characterization of molecules in which pairs of conjugated chains are held in a two-tier (i.e., double decker) geometry by covalent attachment to a rigid scaffold. These scaffolds include [2,2]paracyclophane,[4−7] calix[4]arene,[8] thieno-annelated bicyclo[4.4.1]undecane,[9] 4,5-disubstituted xanthene,[10] a *m*-terphenyl oxacyclophane,[11] and macrocyclic oligothiophenes.[12] For example, pseudo-para (*pp*) disubstituted [2.2]paracyclophanes have been used as a scaffold to explore the interactions between pairs of stacked stilbenes and phenyl ethynylene chromophores, e.g., Figure 1A. Stacked chromophores with relatively short conjugation lengths display a large Stokes shift as a result of absorption by a single tier followed by relaxation of the excited state to a lower energy "phane" electronic state that emits at a significantly higher wavelength.[4] The *pp* [2.2]paracyclophane core has also been incorporated into a number of polymeric structures in which conjugated oligomeric tiers are arranged such that their terminal phenyl rings are held in a stacked manner, e.g., Figure 1B.[13,14] A single example of a polymeric pseudo-ortho (*po*) analog has also been reported.[15] In an elegant extension of this approach to prepare a multitier system, Nakano has demonstrated significant Stokes shifts for polymers in which individual fluorene chromophores are organized in a helical stack.[16]

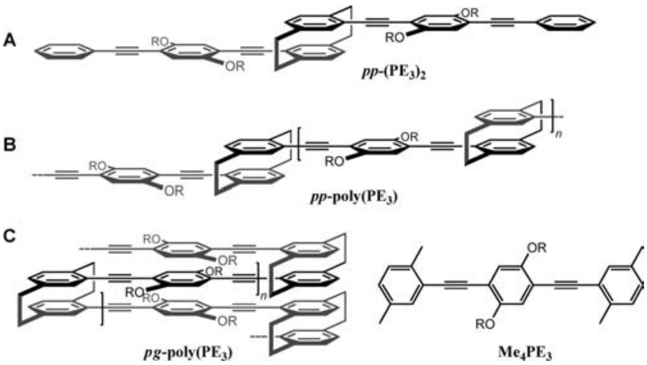

Figure 1. 1,4-Bis(phenylethynyl)-2,5-dialkoxybenzene (PE_3) containing oligomers: (A) pseudo-*para*-[2.2]paracyclophane stacked dimer, ***pp*-(PE$_3$)$_2$** (R = *n*-$C_{12}H_{25}$, ref 4); (B) polymeric analog, ***pp*-poly(PE$_3$)** (R = *n*-$C_{12}H_{25}$, ref 19); (C) pseudo-geminal polymer consisting of an extended stack, ***pg*-poly(PE$_3$)**, and unstacked **Me$_4$PE$_3$**, R = *n*-C_9H_{19}.

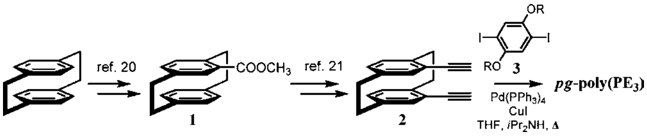

Figure 2. Preparation of ***pg*-poly(PE$_3$)** (R = *n*-C_9H_{19}).

To increase the extent of interaction between conjugated oligomers, we have prepared a new polymeric architecture using pseudo-geminal (*pg*) disubstituted [2.2]paracyclophane as a scaffold. The combination of the U-turn imparted by this core[17] with a linear 1,4-phenylene bis(ethynylene) unit provides a three-ring phenylene ethynylene oligomer ("PE_3") which is held in a stacked arrangement over its entire length in a multitiered assembly, i.e., ***pg*-poly(PE$_3$)**, Figure 1C. The PE_3 tier resembles a segment of a poly(1,4-phenylene ethynylene), PPE, a highly fluorescent class of materials with potential for use in LEDs and sensors,[18] and the stacked arrangement of the PE_3 tiers is similar to the assembly of segments of conjugated polymers in the solid state. Here we compare the optical properties of the pseudo-geminal polymer with its unstacked analogue (**Me$_4$PE$_3$**), the analogous *pp*[19] and *po*[15] polymers, and the model π-stacked dimer (***pp*-(PE$_3$)$_2$**),[4] Figure 1. This comparison establishes the influence of extending the length over which the conjugated units are held in a stacked arrangement (i.e., along the entire length of the oligomer, as opposed to close contact between just the terminal units in the *pp* analog) and the effect of assembling multiple conjugated chains into extended multitier stacks.

4,15-Diethynyl-[2.2]paracyclophane, **2**, was prepared from methyl [2.2]paracyclophanecarboxylate, **1**.[20] Formylation of **1** takes place

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in a regiospecific manner at the pseudo-geminal position, and conversion to the diethynyl analog was achieved according to established procedures, Figure 2.[21] Monomers **2** and 1,4-diiodo-2,5-bis(nonyloxy)benzene, **3**, were subjected to Sonogashira cross-coupling condensation polymerization in the presence of a catalytic amount of $Pd(PPh_3)_4$ and CuI in diisopropylamine-THF. The crude polymer was precipitated by addition of the reaction mixture to methanol and reprecipitated in acetone to give ***pg*-poly(PE_3)** as an orange solid (60% isolated yield). **Me_4PE_3** was prepared as a model for the isolated (i.e., unstacked) tier of the polymer.

The ^1H NMR spectrum of ***pg*-poly(PE_3)** consists of a series of broad peaks with chemical shifts consistent with the expected structure. The breadth of these peaks arises from the rigidity of the polymer in which rotation within each oligomeric tier is severely restricted. The molecular weight of the polymer determined by SEC was 5 kD, with a polydispersity index (PDI) of 1.7 (THF eluent, calibrated against polystyrene standards[22]). This corresponds to an average of eight repeat units in the polymer chain (i.e., eight tiers). The polymer is soluble in common organic solvents ($CHCl_3$, CH_2Cl_2, and toluene) and is easily processed into thin films by drop casting or spin coating.

The UV−visible and fluorescence spectra of ***pg*-poly(PE_3)** were compared to those of the corresponding unstacked model, **Me_4PE_3**, Figure 3. The polymer and unstacked analog have similar absorption maxima at ca. 320 and 365 nm, but the absorption edge of the polymeric analog is red-shifted by ca. 50 nm from that of **Me_4PE_3** and lacks the vibronic structure of the latter. The emission spectrum of the *pg* polymer shows a broad peak which is significantly red-shifted ($\lambda_{max} = 530$) and stronger compared to the spectrum of the linear unstacked model ($\lambda_{max} = 402$).

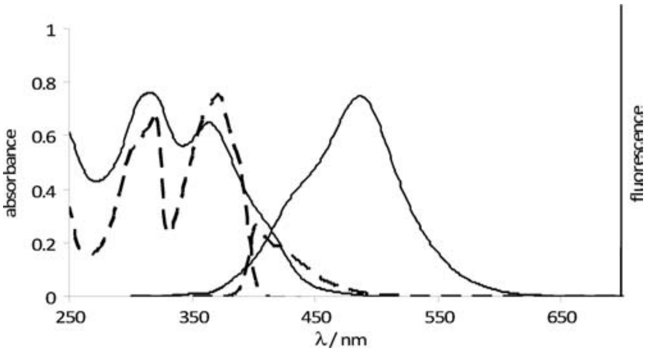

Figure 3. UV−visible and fluorescence spectra of pseudo-geminal cyclophane polymer ***pg*-poly(PE_3)** (solid line) and unstacked model **Me_4PE_3** (dashed line). [PE_3 oligomer] = 1×10^{-5} M in $CHCl_3$, $T = 23$ °C.

Table 1. Absorption and Emission Spectra

	Absorption λ_{max}/nm[a]	Emission λ_{max}/nm[a]	Stokes shift nm[a]
***pg*-poly(PE_3)**	320, 359	530	171
Me_4PE_3	321, 374	402 (413)[d]	28
***pp*-(PE_3)$_2$**[b]	*b*	*b*	*b*
***pp*-poly(PE_3)**[c]	319, 386	414 (438)[d]	28
***po*-poly(PE_3)**[c]	319, 377	411 (434)[d]	34

[a] [Analyte] = 10^{-5} M in $CHCl_3$. [b] Spectra shown in ref 4; λ_{max} not provided. [c] Reference 15. [d] Vibronic peaks.

While the large Stokes shift of the *pg* polymer (171 nm) relative to that of the linear unstacked oligomer (28 nm) can be explained by energy transfer to a phane electronic state, this behavior is in sharp contrast to that of all of the other PE_3-containing analogs. The *pp* stacked dimer ***pp*-(PE_3)$_2$**,[4] *pp* polymer,[15] and *po* polymer[15] all display absorption and emission spectra which are similar to that of the linear unstacked model **Me_4PE_3**, Table 1 (i.e., absorption λ_{max} in the range of 380 ± 5 nm; emission maxima at 408 ± 6 nm, and Stokes shifts of 31 ± 3 nm). In each of these cases, the excited state of a single conjugated chromophoric tier is sufficiently stable that there is no driving force for energy transfer to a phane state. In these previous studies there is limited overlap between the conjugated tiers, and large Stokes shifts are observed only for shorter chromophores. However, this does not reflect the extended nature of the interactions between segments of conjugated polymers in the solid state. The large Stokes shift of ***pg*-poly(PE_3)** suggests that interchain interactions of the chromophoric tiers over the entire length of the conjugated chains, and stacking in an extended multitier arrangement, provide for stabilization of a phane state which is not available to the other regioisomers of the polymer (e.g., *pp*, *po*), the *pp* stacked dimer, or unstacked analogs.

The pseudo-geminal disubstituted [2.2]paracyclophane core constitutes a versatile scaffold that provides opportunities to vary the stacking of conjugated tiers in two dimensions, akin to the organization of segments of conjugated polymers in the solid state (i.e., through modification of the conjugation length of the tiers and by variation of the number of tiers held in a stack). The exploration of the effect of these structural parameters on the optical properties of such ladder polymers will provide additional insights into the evolution of electronic structure upon bringing conjugated systems into close proximity.

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Supporting Information Available: Synthetic schemes and characterization data are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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