

π -Stacked Oligo(phenylene vinylene)s Based on Pseudo-Geminal Substituted [2.2]Paracyclophanes: Impact of Interchain Geometry and Interactions on the Electronic Properties**

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The design of conjugated organic semiconducting materials for use in field-effect transistors, light-emitting diodes, and solar cells requires a detailed understanding of the relationships between molecular geometry, interchain interactions, and electronic properties.^[1] The investigation of molecules that consist of pairs of stacked conjugated chains held in well-defined arrangements by a [2.2]paracyclophane (CP)^[2] core is a useful strategy to explore interactions between π systems. For example, Bazan et al. have performed extensive spectroscopic and theoretical analyses of stacked phenylene vinylenes (PV) based on pseudo-*para* (*pp*) analogues of [2.2]paracyclophane.^[3] When two stilbene segments (PV₂) are stacked in this fashion, that is, *pp*-CP(PV₂)₂ in Figure 1, the fluorescence spectrum is dominated by a broad featureless peak that is significantly red-shifted from the absorption maximum by virtue of the presence of a localized “phane state”.^[3] However, the fluorescence spectrum of the analogue with longer stacked 1,4-distyrylbenzene (PV₃) segments, that is, *pp*-CP-

(PV₃)₂, resembles that of the corresponding unstacked conjugated oligomer (Me₂PV₃). While the *pp* and pseudo-*ortho* (*po*) analogues hold the two conjugated chains in close proximity, only the phenylene rings within the paracyclophane core are stacked. As a result, there are minimal interactions between the two conjugated segments as soon as their lengths are increased.

The pseudo-geminal (*pg*) substitution pattern of [2.2]paracyclophane holds substituents on each ring directly atop one another. Such stacking of conjugated units leads to facile intramolecular photochemical cycloadditions,^[4–7] and new electronic transitions in multi-decker stacks.^[8] The opportunity to prepare new materials containing the cyclophane core has recently attracted increased attention.^[9,10] Here, we explore the absorption and fluorescence spectra of stacked PV oligomers that are based on the *pg*-CP core: the stacked stilbene *pg*-CP(PV₂)₂ and the analogues distyrylbenzene, *pg*-CP(PV₃)₂. We compare the spectroscopic and electronic properties of the *pg* compounds to those of their *pp* and *po* analogues and the corresponding isolated oligomers.

Conjugated arms were installed on the *pg* core by a Heck reaction between 4,15-divinyl[2.2]paracyclophane^[5] and 1-iodobenzene or 1-iodo-4-styrylbenzene to afford *pg*-CP[PV₂]₂ and *pg*-CP[PV₃]₂, respectively (see Figure 2 and the Supporting Information for experimental details). The ¹H NMR spectra of the products are consistent with conformations in which the arms are oriented away from the neighboring ethano bridge, as previously elucidated for 4,15-divinyl-[2.2]paracyclophane.^[5]

The absorption maximum of *pg*-CP[PV₂]₂ (4.19 eV) is only slightly blue-shifted relative to that of the isolated analogue Me₂PV₂ (4.17 eV), see Figure 3 A and Table 1. However, a major difference between the spectra of these compounds is the presence of a shoulder arising from a contribution at 3.38 eV for the stacked molecule. Similar features are observed in the absorption spectrum of the longer stacked compound *pg*-CP[PV₃]₂ (Figure 3 B).

The emission spectrum of Me₂PV₂ presents a distinct vibronic progression. On the other hand, the emission spectrum of *pg*-CP[PV₂]₂ displays a broad, structureless peak (2.86 eV) that is red-shifted by about 0.2 eV compared to the corresponding *pp* and *po* analogues.^[3a] The fluorescence spectrum of the longer stacked analogue, *pg*-CP[PV₃]₂, is similar to that of the shorter analogue but with a significant tail by virtue of a strong contribution at 2.56 eV, which is clearly apparent in the difference spectrum shown as an inset in Figure 3 B. Importantly, this broad tail is absent from the

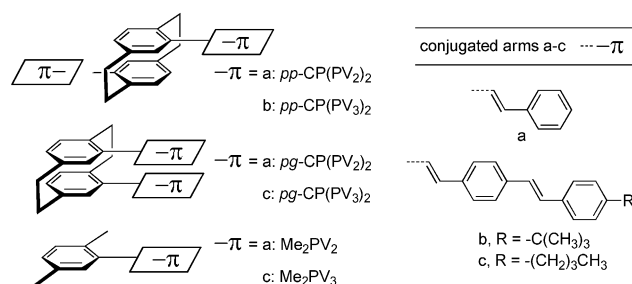


Figure 1. [2.2]Paracyclophane oligo(phenylene vinylene)s based on a pseudo-*para* (*pp*), pseudo-geminal (*pg*) core, and the isolated model chromophores (Me₂PV_n).

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[**] This work was supported by NSF awards ECCE-0437925, DMR-0120967 and CHE-0946869.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201205738>.

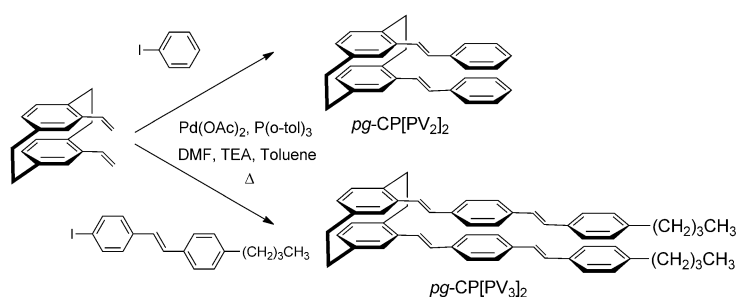


Figure 2. Synthesis of the pseudo-geminal compounds, *pg*-CP[PV₂]₂ and *pg*-CP-[PV₃]₂.

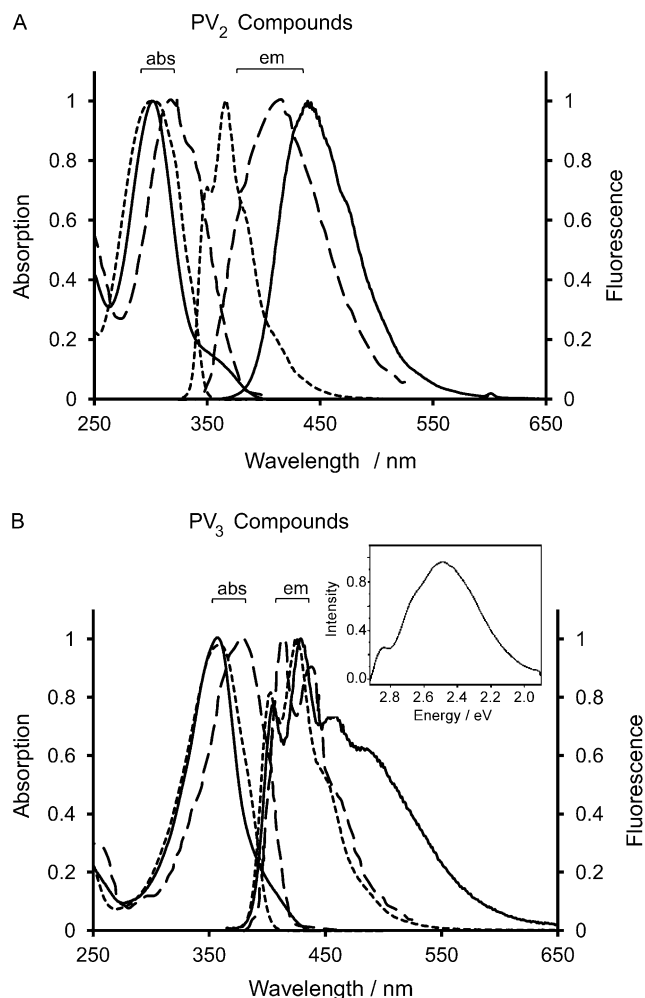


Figure 3. Normalized UV/Vis and fluorescence spectra (CHCl₃, 23 °C) of A) *pg*-CP[PV₂]₂ (solid line; $c = 1.3 \times 10^{-6}$ M), Me₂PV₂ (dotted line; $c = 2.5 \times 10^{-6}$ M), and *pp*-CP[PV₂]₂ (dashed line) and B) *pg*-CP[PV₃]₂ (solid line; $c = 1.5 \times 10^{-6}$ M), Me₂PV₃ (dotted line; $c = 3.0 \times 10^{-6}$ M), and *pp*-CP[PV₃]₂ (dashed line; abs = absorption and em = emission). The inset in (B) depicts the difference in emission spectra between *pg*-CP[PV₃]₂ and Me₂PV₃ on an energy scale. The spectra of *pp* compounds are adapted from ref. [3a]; those of the *po* analogues are similar.

fluorescence spectra of the unstacked oligomer Me₂PV₃ and the corresponding *pp* and *po* analogues (see Figure 3 and the Supporting Information).^[3a] Thus, the spectroscopic data reveal significant differences between the electronic struc-

tures of the *pg* molecules and their *pp* and *po* counterparts. To understand the origin of these differences, we performed time-dependent density functional theory (TD-DFT) calculations on the stacked and isolated systems.

The TD-DFT-calculated excited-state energies and oscillator strengths are provided in Table 2 (see the Supporting Information for details). The wavefunction characteristics of the S₀→S₁ and S₁→S₀ transitions are illustrated in Figure 4. In Me₂PV₂ and Me₂PV₃, the lowest TD-DFT absorption corresponds to the S₀→S₁ transition and is dominated by

Table 1: Main characteristics of the absorption and emission spectra.

Molecule	Absorption maxima [nm] ^[a] (eV) ^[b]	Emission maxima [nm] ^[a] (eV) ^[b]
Me ₂ PV ₂	297 (4.17)	345, 359, 381 (3.56, 3.39, 3.22)
<i>pg</i> -CP[PV ₂] ₂	296, 358 ^[c] (4.19, 3.38)	435 (2.86)
Me ₂ PV ₃	352 (3.52)	396, 416, 440 (3.09, 2.92, 2.75)
<i>pg</i> -CP[PV ₃] ₂	350, 404 ^[c] (3.54, 3.07)	404, 427, 446, 481 (3.06, 2.90, 2.73, 2.56)

[a] Peaks in spectra, Figure 3. [b] Energies (eV) computed from deconvoluted spectra (see the Supporting Information). [c] Shoulder.

a simple HOMO→LUMO excitation (HOMO/LUMO = highest/lowest occupied/unoccupied molecular orbital). The origins of the first absorption band in *pp*-CP[PV₂]₂ and *pp*-CP[PV₃]₂ are different, being related to S₀→S₂ and S₀→S₁ transitions, respectively. For smaller analogues, the S₂ states of the *pp* compounds are primarily localized on a single segment and may be referred to as local states.

We note that the difference in energy between the S₁ and S₂ states of *pp*-CP[PV₂]₂ is small (0.1 eV, Table 2); thus, the weak transition to the S₁ state is masked by the S₂ transition in the absorption spectrum.

The picture changes markedly in the *pg* compounds. Here, the absorption spectra are dominated by the S₀→S₂ transition irrespective of the length of the conjugated arms and correspond to the mixing of arm-localized and cyclophane-core-localized (phane-state) excitations (see the Supporting Information). The S₁ state has a weak oscillator strength and is located below the S₂ state by 0.5 eV in *pg*-CP[PV₂]₂ and 0.3 eV in *pg*-CP[PV₃]₂, which is consistent with the appearance of the low-energy shoulders in the absorption spectra. Figure 4 shows how the S₁ states of the *pg* compounds, in contrast to the *pp* analogues, are delocalized over the entire molecules and correspond to a linear combination of intra-arm localized excitations and interarm charge-transfer excitations (see the Supporting Information).^[11,12]

The results of these calculations allow us to propose the following scenario. In *pp*-CP[PV₂]₂, absorption into the S₂ state is followed by internal conversion to the S₁ state, with

Table 2: DFT estimates of vertical absorption (in the S_0 -state geometry) and emission energies (in the S_1 -state relaxed geometry), ground-state relaxation energies upon emission (λ_{gs}), and 0–0 emission energies. The oscillator strengths are given in parentheses. All energies are in electron volts.^[a]

Molecule	Excited state	S_0 state	Relaxed S_1 state	λ_{gs}	0–0 Emission energy
Me_2PV_2	S_1	4.4 (0.89)	3.2 (0.82)	0.5	3.7
$pp\text{-CP}[\text{PV}_2]_2$	S_1	4.1 (0.02)	3.3 (0.01)	0.4	3.7
	S_2	4.2 (1.26)			
$pg\text{-CP}[\text{PV}_2]_2$	S_1	3.7 (0.01)	2.1 (0.01)	0.7	2.8
	S_2	4.2 (0.44)			
Me_2PV_3	S_1	3.7 (1.81)	3.0 (1.92)	0.1	3.1
$pp\text{-CP}[\text{PV}_3]_2$	S_1	3.6 (3.48)	2.9 (2.30)	0.3	3.2
$pg\text{-CP}[\text{PV}_3]_2$	S_1	3.3 (0.02)	2.0 (0.01)	0.5	2.5
	S_2	3.6 (1.61)			

[a] Computed at the $\omega\text{B97X-D/6-31g}^{**}$ level for the transoid conformation of Me_2PV_3 and the transoid–transoid conformations of $pg\text{-CP}[\text{PV}_3]_2$ and $pp\text{-CP}[\text{PV}_3]_2$.

the $S_1 \rightarrow S_0$ emission dominated by a localized phane-state contribution (see Figure 4A). In contrast, the pg isomer undergoes a marked geometry relaxation in the S_1 state that results in a decrease of the distance between the stacked conjugated segments. The relaxed S_1 state (Figure 4B) is delocalized over the entire molecule and has larger contributions from intersegment charge-transfer excitations than from intrasegment localized excitations. Thus, the S_1 state of the pg compound corresponds to an excimer-like state delocalized over the entire molecule, in contrast to the phane-localized S_1 state of the pp and po analogues. The characteristics of such an excimer state are consistent with the experimental observation of a broad, featureless emission band that is

strongly red-shifted compared to the emission maxima in the pp , po , and isolated analogues.

Turning to the longer $\text{CP}[\text{PV}_3]_2$ compounds, an even more striking difference in the nature of the S_1 state is apparent, when comparing the pg and pp analogues. In $pp\text{-CP}[\text{PV}_3]_2$, the S_1 state is strictly confined to a single distyrylbenzene segment (Figure 4C). In contrast, the S_1 state of $pg\text{-CP}[\text{PV}_3]_2$ is delocalized over the entire molecule (Figure 4D) and presents a similar excimer nature as the S_1 state of $pg\text{-CP}[\text{PV}_2]_2$. This is consistent with the presence of the broad shoulder in the emission spectrum (inset of Figure 3B), unlike the situation for the isolated pp and po analogues that display no sign of excimer emission. Thus, the fully delocalized excimeric nature of the S_1 state is observed only when the conjugated chromophores stack along their entire length.

To summarize, the excimeric emission of pg -stacked oligo(phenylene vinylene)s is in contrast to emission from a phane-state in $pp\text{-CP}(\text{PV}_2)_2$ and from a localized excited state in $pp\text{-CP}(\text{PV}_3)_2$. The stacking of conjugated oligomers in a well-defined manner along their entire length by virtue of the $pg\text{-CP}$ scaffold demonstrates the impact of extended interchain interactions on the photophysics of π -stacked systems.

Received: July 18, 2012

Revised: September 4, 2012

Published online: October 12, 2012

Keywords: conjugation · density functional calculations · photophysics · π interactions · stacking interactions

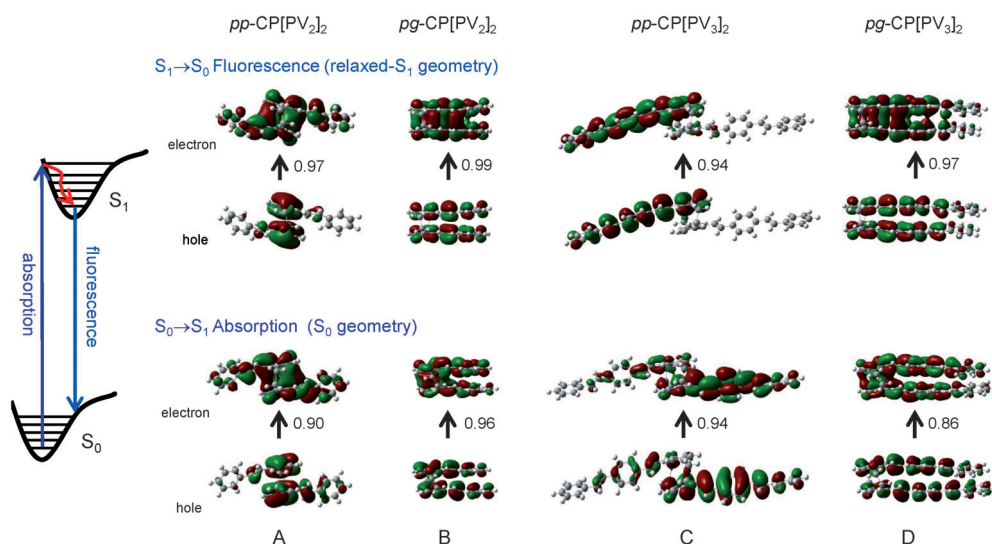


Figure 4. Natural transition orbitals (NTOs) corresponding to the S_1 (relaxed excited state) $\rightarrow S_0$ transitions (top panel) and $S_0 \rightarrow S_1$ (ground-state geometry) transitions (bottom panel). The contributions of the electron–hole excitations to the transitions are given.

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