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

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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.<sup>[1]</sup> The investigation of molecules that consist of pairs of stacked conjugated chains held in welldefined arrangements by a [2.2]paracyclophane (CP)<sup>[2]</sup> core is a useful strategy to explore interactions between  $\pi$  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.<sup>[3]</sup> When two stilbene segments (PV<sub>2</sub>) are stacked in this fashion, that is, pp-CP(PV<sub>2</sub>)<sub>2</sub> 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".<sup>[3]</sup> However, the fluorescence spectrum of the analogue with longer stacked 1,4-distyrylbenzene (PV<sub>3</sub>) segments, that is, pp-CP-



**Figure 1.** [2.2]Paracyclophane oligo(phenylene vinylene)s based on a pseudo-*para (pp)*, pseudo-geminal (*pg*) core, and the isolated model chromophores ( $Me_2PV_n$ ).

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tems. 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,<sup>[4–7]</sup> and new electronic transitions in multi-decker stacks.<sup>[8]</sup> The opportunity to prepare new materials containing the cyclophane core

their lengths are increased.

has recently attracted increased attention.<sup>[9,10]</sup> 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(PV<sub>2</sub>)<sub>2</sub> and the analogoues distyrylbenzene, *pg*-CP(PV<sub>3</sub>)<sub>2</sub>. We compare the spectroscopic and electronic properties of the *pg* compounds to those of their *pp* and *po* analogues and the corresponding isolated oligomers.

 $(PV_3)_2$ , resembles that of the corresponding unstacked conjugated oligomer (Me<sub>2</sub>PV<sub>3</sub>). While the *pp* and pseudo-*ortho* 

(po) analogues hold the two conjugated chains in close

proximity, only the phenylene rings within the paracyclo-

phane core are stacked. As a result, there are minimal

interactions between the two conjugated segments as soon as

Conjugated arms were installed on the pg core by a Heck reaction between 4,15-divinyl[2.2]paracyclophane<sup>[5]</sup> and 1iodobenzene or 1-iodo-4-styrylbenzene to afford pg-CP[PV<sub>2</sub>]<sub>2</sub> and pg-CP[PV<sub>3</sub>]<sub>2</sub>, respectively (see Figure 2 and the Supporting Information for experimental details). The <sup>1</sup>H 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.<sup>[5]</sup>

The absorption maximum of pg-CP[PV<sub>2</sub>]<sub>2</sub> (4.19 eV) is only slightly blue-shifted relative to that of the isolated analogue Me<sub>2</sub>PV<sub>2</sub> (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[PV<sub>3</sub>]<sub>2</sub> (Figure 3 B).

The emission spectrum of  $Me_2PV_2$  presents a distinct vibronic progression. On the other hand, the emission spectrum of pg-CP[PV<sub>2</sub>]<sub>2</sub> 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.<sup>[3a]</sup> The fluorescence spectrum of the longer stacked analogue, pg-CP[PV<sub>3</sub>]<sub>2</sub>, 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 3B. Importantly, this broad tail is absent from the



**Figure 2.** Synthesis of the pseudo-geminal compounds, pg-CP[PV<sub>2</sub>]<sub>2</sub> and pg-CP-[PV<sub>3</sub>]<sub>2</sub>.



**Figure 3.** Normalized UV/Vis and fluorescence spectra (CHCl<sub>3</sub>, 23 °C) of A) *pg*-CP[PV<sub>2</sub>]<sub>2</sub> (solid line;  $c=1.3 \times 10^{-6}$  M), Me<sub>2</sub>PV<sub>2</sub> (dotted line;  $c=2.5 \times 10^{-6}$  M), and *pp*-CP[PV<sub>2</sub>]<sub>2</sub> (dashed line) and B) *pg*-CP[PV<sub>3</sub>]<sub>2</sub> (solid line;  $c=1.5 \times 10^{-6}$  M), Me<sub>2</sub>PV<sub>3</sub> (dotted line;  $c=3.0 \times 10^{-6}$  M), and *pp*-CP[PV<sub>3</sub>]<sub>2</sub> (dashed line;  $a=3.0 \times 10^{-6}$  M), and *pp*-CP[PV<sub>3</sub>]<sub>2</sub> (dashed line; a=b sorption and em=emission). The inset in (B) depicts the difference in emission spectra between *pg*-CP[PV<sub>3</sub>]<sub>2</sub> and Me<sub>2</sub>PV<sub>3</sub> 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  $Me_2PV_3$  and the corresponding *pp* and *po* analogues (see Figure 3 and the Supporting Information).<sup>[3a]</sup> Thus, the spectroscopic data reveal significant differences between the electronic structures 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  $S_0 \rightarrow S_1$  and  $S_1 \rightarrow S_0$ transitions are illustrated in Figure 4. In Me<sub>2</sub>PV<sub>2</sub> and Me<sub>2</sub>PV<sub>3</sub>, the lowest TD-DFT absorption corresponds to the  $S_0 \rightarrow S_1$  transition and is dominated by

Table 1	Main	characteristics	of	the	absor	ntion	and	emission	spectra
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Molecule	Absorption maxima [nm <sup>[a]</sup> (eV) <sup>[b]</sup> ]	Emission maxima [nm <sup>[a]</sup> (eV) <sup>[b]</sup> ]
$Me_2PV_2$	297 (4.17)	345, 359, 381 (3.56, 3.39, 3.22)
pg-CP[PV <sub>2</sub> ] <sub>2</sub>	296, 358 <sup>[c]</sup> (4.19, 3.38)	435 (2.86)
$Me_2PV_3$	352 (3.52)	396, 416, 440 (3.09, 2.92, 2.75)
pg-CP[PV <sub>3</sub> ] <sub>2</sub>	350, 404 <sup>[c]</sup> (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 $\rightarrow$ LUMO excitation (HOMO/LUMO = highest/lowest occupied/unoccupied molecular orbital). The origins of the first absorption band in *pp*-CP[PV<sub>2</sub>]<sub>2</sub> and *pp*-CP[PV<sub>3</sub>]<sub>2</sub> are different, being related to S<sub>0</sub> $\rightarrow$ S<sub>2</sub> and S<sub>0</sub> $\rightarrow$ S<sub>1</sub> transitions, respectively. For smaller analogues, the S<sub>2</sub> 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  $S_1$  and  $S_2$  states of pp-CP[PV<sub>2</sub>]<sub>2</sub> is small (0.1 eV, Table 2); thus, the weak transition to the  $S_1$  state is masked by the  $S_2$  transition in the absorption spectrum.

The picture changes markedly in the pg compounds. Here, the absorption spectra are dominated by the  $S_0 \rightarrow S_2$  transition irrespective of the length of the conjugated arms and correspond to the mixing of arm-localized and cyclophanecore-localized (phane-state) excitations (see the Supporting Information). The S<sub>1</sub> state has a weak oscillator strength and is located below the S<sub>2</sub> state by 0.5 eV in pg-CP[PV<sub>2</sub>]<sub>2</sub> and 0.3 eV in pg-CP[PV<sub>3</sub>]<sub>2</sub>, which is consistent with the appearance of the low-energy shoulders in the absorption spectra. Figure 4 shows how the S<sub>1</sub> states of the pg compounds, in contrast to the pp analogues, are delocalized over the entire molecules and correspond to a linear combination of intraarm localized excitations and interarm charge-transfer excitations (see the Supporting Information).<sup>[11,12]</sup>

The results of these calculations allow us to propose the following scenario. In pp-CP[PV<sub>2</sub>]<sub>2</sub>, absorption into the S<sub>2</sub> state is followed by internal conversion to the S<sub>1</sub> state, with

**Table 2:** DFT estimates of vertical absorption (in the S<sub>0</sub>-state geometry) and emission energies (in the S<sub>1</sub>-state relaxed geometry), ground-state relaxation energies upon emission ( $\lambda_{gs}$ ), and 0–0 emission energies. The oscillator strengths are given in parentheses. All energies are in electron volts.<sup>[a]</sup>

Molecule	Excited state	S <sub>0</sub> state	Relaxed $S_1$ state	$\lambda_{\rm gs}$	0–0 Emission energy
$Me_2PV_2$	<b>S</b> <sub>1</sub>	4.4 (0.89)	3.2 (0.82)	0.5	3.7
<i>pp</i> -CP[PV <sub>2</sub> ] <sub>2</sub>	S <sub>1</sub> S <sub>2</sub>	4.1 (0.02) 4.2 (1.26)	3.3 (0.01)	0.4	3.7
pg-CP[PV <sub>2</sub> ] <sub>2</sub>	S <sub>1</sub> S <sub>2</sub>	3.7 (0.01) 4.2 (0.44)	2.1 (0.01)	0.7	2.8
${\sf Me}_2{\sf PV}_3$	S <sub>1</sub>	3.7 (1.81)	3.0 (1.92)	0.1	3.1
$pp-CP[PV_3]_2$	S <sub>1</sub>	3.6 (3.48)	2.9 (2.30)	0.3	3.2
pg-CP[PV <sub>3</sub> ] <sub>2</sub>	S <sub>1</sub> S <sub>2</sub>	3.3 (0.02) 3.6 (1.61)	2.0 (0.01)	0.5	2.5

[a] Computed at the  $\omega$ B97X-D/6-31g<sup>\*\*</sup> level for the transoid conformation of Me<sub>2</sub>PV<sub>3</sub> and the transoid–transoid conformations of *pg*-CP[PV<sub>3</sub>]<sub>2</sub> and *pp*-CP[PV<sub>3</sub>]<sub>2</sub>.

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  $S_1$ 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  $CP[PV_3]_2$  compounds, an even more striking difference in the nature of the S<sub>1</sub> state is apparent, when comparing the *pg* and *pp* analogues. In *pp*-CP[PV<sub>3</sub>]<sub>2</sub>, the S<sub>1</sub> state is strictly confined to a single distyrylbenzene segment (Figure 4C). In contrast, the S<sub>1</sub> state of *pg*-CP[PV<sub>3</sub>]<sub>2</sub> is delocalized over the entire molecule (Figure 4D) and presents a similar excimer nature as the S<sub>1</sub> state of *pg*-CP[PV<sub>2</sub>]<sub>2</sub>. 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<sub>1</sub> 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-CP(PV<sub>2</sub>)<sub>2</sub> and from a localized excited state in pp-CP(PV<sub>3</sub>)<sub>2</sub>. The stacking of conjugated oligomers in a well-defined manner along their entire length by virtue of the pg-CP scaffold demonstrates the impact of extended interchain interactions on the photophysics of  $\pi$ -stacked systems.

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*Figure 4.* Natural transition orbitals (NTOs) corresponding to the S<sub>1</sub> (relaxed excited state) $\rightarrow$ S<sub>0</sub> transitions (top panel) and S<sub>0</sub> $\rightarrow$ S<sub>1</sub> (ground-state geometry) transitions (bottom panel). The contributions of the electron-hole excitations to the transitions are given.

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