Electronic Structure

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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 (PV_2) are stacked in this fashion, that is, *pp*-CP$(PV_2)_2$ 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 (PV_3) segments, that is, *pp*-CP$(PV_3)_2$, resembles that of the corresponding unstacked conjugated oligomer (Me_2PV_3). 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.

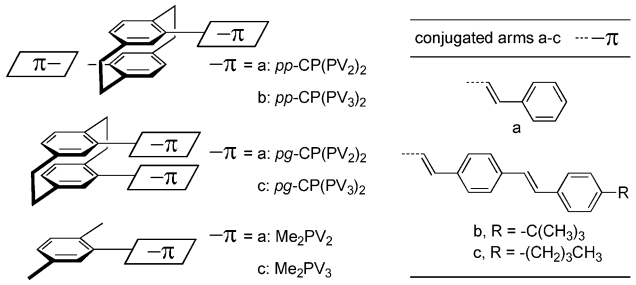

Figure 1. [2.2]Paracyclophane oligo(phenylene vinylene)s based on a pseudo-*para* (*pp*), pseudo-geminal (*pg*) core, and the isolated model chromophores (Me_2PV_n).

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$(PV_2)_2$ and the analogoues distyrylbenzene, *pg*-CP$(PV_3)_2$. 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$[PV_2]_2$ and *pg*-CP$[PV_3]_2$, respectively (see Figure 2 and the Supporting Information for experimental details). The ^{1}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.[5]

The absorption maximum of *pg*-CP$[PV_2]_2$ (4.19 eV) is only slightly blue-shifted relative to that of the isolated analogue Me_2PV_2 (4.17 eV), see Figure 3A 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$[PV_3]_2$ (Figure 3B).

The emission spectrum of Me_2PV_2 presents a distinct vibronic progression. On the other hand, the emission spectrum of *pg*-CP$[PV_2]_2$ 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$[PV_3]_2$, 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 3B. Importantly, this broad tail is absent from the

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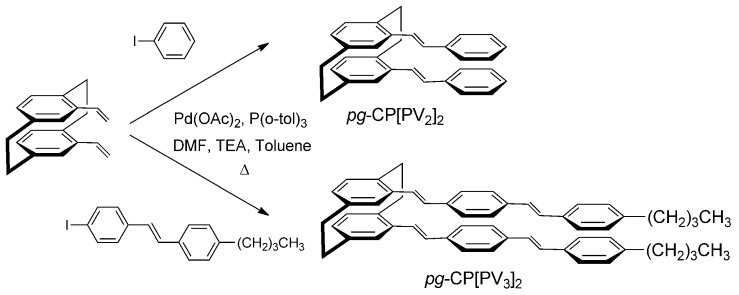

Figure 2. Synthesis of the pseudo-geminal compounds, *pg*-CP[PV_2]$_2$ and *pg*-CP[PV_3]$_2$.

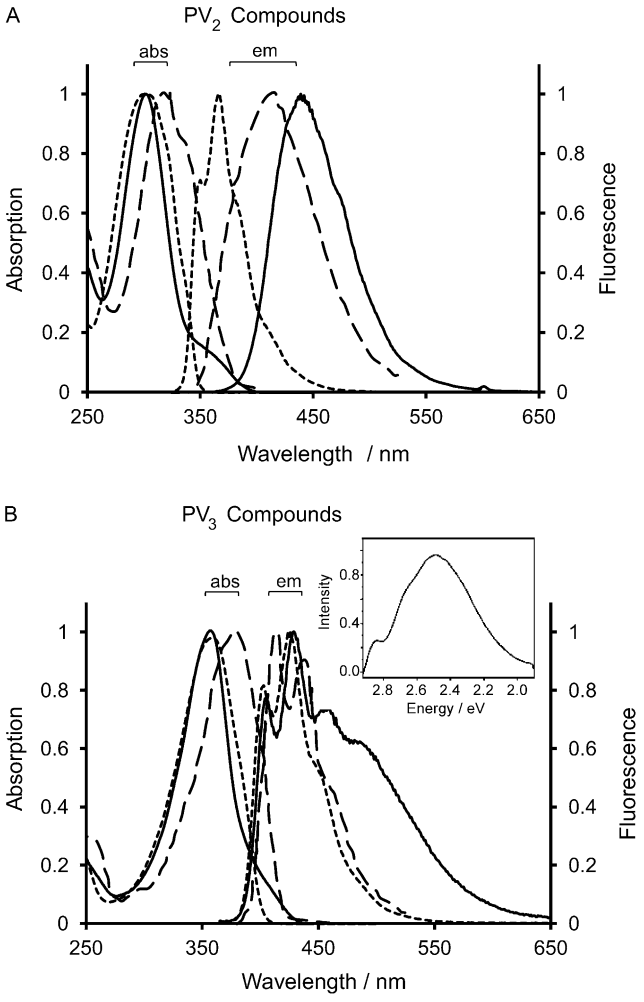

Figure 3. Normalized UV/Vis and fluorescence spectra ($CHCl_3$, 23 °C) of A) *pg*-CP[PV_2]$_2$ (solid line; $c = 1.3\times10^{-6}$ M), Me_2PV_2 (dotted line; $c = 2.5\times10^{-6}$ M), and *pp*-CP[PV_2]$_2$ (dashed line) and B) *pg*-CP[PV_3]$_2$ (solid line; $c = 1.5\times10^{-6}$ M), Me_2PV_3 (dotted line; $c = 3.0\times10^{-6}$ M), and *pp*-CP[PV_3]$_2$ (dashed line; abs = absorption and em = emission). The inset in (B) depicts the difference in emission spectra between *pg*-CP[PV_3]$_2$ and Me_2PV_3 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).[3a] 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_2PV_2 and Me_2PV_3, the lowest TD-DFT absorption corresponds to the $S_0\rightarrow S_1$ 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_2PV_2	297 (4.17)	345, 359, 381 (3.56, 3.39, 3.22)
pg-CP[PV_2]$_2$	296, 358[c] (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_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[PV_2]$_2$ and *pp*-CP[PV_3]$_2$ are different, being related to $S_0\rightarrow S_2$ and $S_0\rightarrow S_1$ transitions, respectively. For smaller analogues, the S_2 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_2]$_2$ 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 cyclophane-core-localized (phane-state) excitations (see the Supporting Information). The S_1 state has a weak oscillator strength and is located below the S_2 state by 0.5 eV in *pg*-CP[PV_2]$_2$ and 0.3 eV in *pg*-CP[PV_3]$_2$, which is consistent with the appearance of the low-energy shoulders in the absorption spectra. Figure 4 shows how the S_1 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[PV_2]$_2$, absorption into the S_2 state is followed by internal conversion to the S_1 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-CP[PV_2]$_2$	S_1 S_2	4.1 (0.02) 4.2 (1.26)	3.3 (0.01)	0.4	3.7
pg-CP[PV_2]$_2$	S_1 S_2	3.7 (0.01) 4.2 (0.44)	2.1 (0.01)	0.7	2.8
Me_2PV_3	S_1	3.7 (1.81)	3.0 (1.92)	0.1	3.1
pp-CP[PV_3]$_2$	S_1	3.6 (3.48)	2.9 (2.30)	0.3	3.2
pg-CP[PV_3]$_2$	S_1 S_2	3.3 (0.02) 3.6 (1.61)	2.0 (0.01)	0.5	2.5

[a] Computed at the ωB97X-D/6-31g** level for the transoid conformation of Me_2PV_3 and the transoid–transoid conformations of *pg*-CP[PV_3]$_2$ and *pp*-CP[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 CP[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*-CP[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*-CP[PV_3]$_2$ is delocalized over the entire molecule (Figure 4D) and presents a similar excimer nature as the S_1 state of *pg*-CP[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*-CP(PV_2)$_2$ and from a localized excited state in *pp*-CP(PV_3)$_2$. 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 π-stacked systems.

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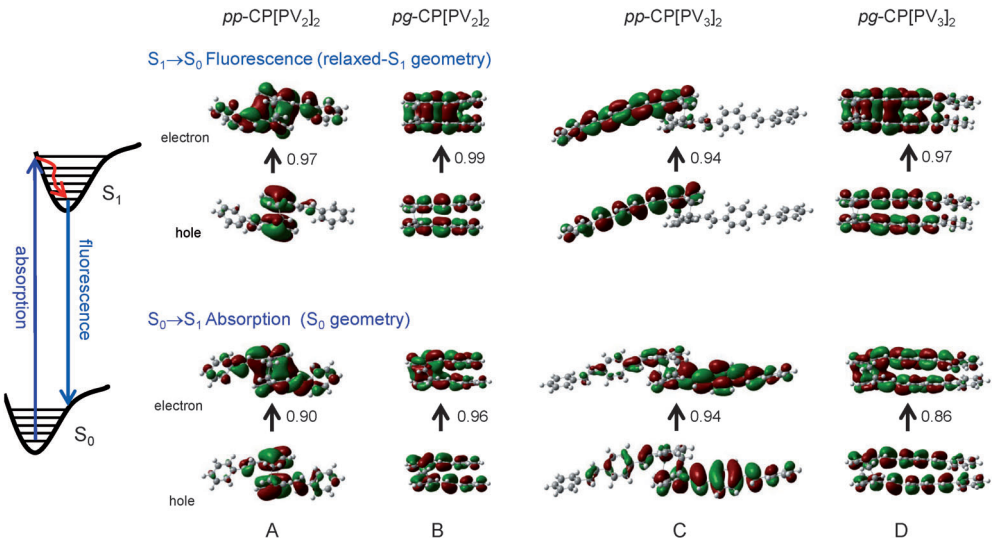

Figure 4. Natural transition orbitals (NTOs) corresponding to the S_1 (relaxed excited state)→S_0 transitions (top panel) and $S_0 \rightarrow S_1$ (ground-state geometry) transitions (bottom panel). The contributions of the electron–hole excitations to the transitions are given.

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