Conjugated Oligomers

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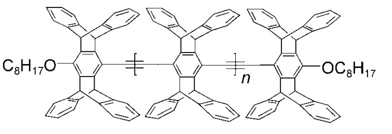
# Pentiptycene-Derived Oligo(*p*-phenyleneethynylene)s: Conformational Control, Chain-Length Effects, Localization of Excitation, and Intrachain Resonance Energy Transfer**

*Jye-Shane Yang,* Jyu-Lun Yan, Cheng-Kai Lin, Chih-Yuan Chen, Zhen-Yu Xie, and Chung-Hsuan Chen*

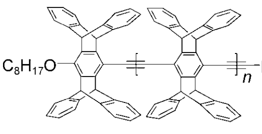
Conjugated polymers (CPs) have attracted substantial attention because of their high potential as materials for optoelectronic devices such as light-emitting diodes and photovoltaic cells.[1–3] To engineer systems with specific electronic properties, a detailed understanding of the structure–property relationships of CPs is essential. However, the poorly defined chain length, chain conformation, and structural defects, as well as the multiple-chromophoric nature[4] of CPs often complicate data analysis and thus make any further investigation difficult. In this context, complementary evidence from the corresponding monodisperse single-chromophore-based conjugated oligomers might offer a solution. We report herein an intriguing example of the concept of torsion-induced excitation localization.

Torsion along the conjugated backbone of CPs is known to have a dramatic impact on optical bandgap and electron mobility because of a decrease in conjugation interactions.[5,6] It is also widely accepted that a flexible CP chain can be considered as an ensemble of chromophores of different lengths because of the conformational disorder of large torsion angles,[7] and, consequently, excitation delocalization is dominated by resonance energy transfer (ET; Förster-type energy transfer or hopping) among the chromophores.[8] Recent quantum chemical calculations further revealed that a medium torsion angle ($\leq 50°$) is sufficient to confine the excitation within a short subunit of CPs.[9] Nevertheless, the concept of torsion-induced localization of excitation and the resulting intrachain ET have not yet been verified with structurally well-defined conjugated oligomers, presumably because of the difficulties in conformational control[10] and in prevention of excited-state torsional relaxation[11] for the twisted conformers.

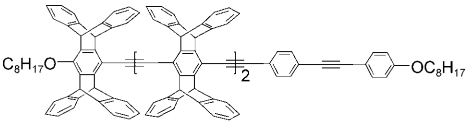
Our recent work[12,13] on the pentiptycene-derived oligo(*p*-phenyleneethynylene)s (OPEs) **1** and **2** have revealed



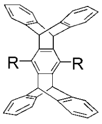
**1**: *n* = 1 **2**: *n* = 2 **3**: *n* = 3 **4**: *n* = 4 **5**: *n* = 5



**7**: *n* = 1 **8**: *n* = 2



**6**



**9**: R = Br **10**: R = CCH

that these systems are excellent candidates for investigation of the concept of torsion-induced localization of excitation. Two distinct fluorescing states, which correspond to excited conformers of small and large torsion angles, have been identified for both **1** and **2**. To simplify the discussion, we refer to the two fluorescing states as the planar (P) and the twisted (T) excited states, respectively. The planar excited state can be generated by selective excitation of the planar conformers, which dominate the longer-wavelength region of the absorption profile, or through torsional relaxation of a twisted Franck–Condon excited state at room temperature. The twisted excited state can be generated and captured by selective excitation of the twisted conformers with short-wavelength light (e.g., 302 nm) in a 2-methyltetrahydrofuran (MTHF) glass at 80 K. This procedure relies not only on the neighboring noncovalent pentiptycene–pentiptycene interactions that favor the twisted form at low temperatures, but also on the large resistance to rotation of the pentiptycene groups in a frozen glass. One particularly interesting but unexplained observation[12] is the same fluorescence profiles recorded for the twisted excited states of **1** and **2** (see below), despite their different chain lengths. We postulated that this observation is due to localized excited states with the excitation confined in a common segment, as the calculated torsion angle (ca. 75°)[12] for the twisted states is larger than the predicted threshold of 50°[9] for localization of excitation. We provide herein the evidence to confirm this hypothesis, through the chain-length effect of these systems that contain 3–7 pentiptycene units (i.e., OPEs **1**–**5**) and through the occurrence of resonance ET in the pentiptycene–phenylene hybrid compound **6**.

The OPEs **3**–**6** were prepared through a series of Sonogashira cross-coupling reactions of the known pentiptycene

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[*] Prof. J.-S. Yang, C.-K. Lin, C.-Y. Chen, Z.-Y. Xie
Department of Chemistry, National Taiwan University
Taipei, Taiwan, 10617 (Republic of China)
Fax: (+886) 223636359
E-mail: jsyang@ntu.edu.tw

J.-L. Yan
Department of Chemistry, National Central University
Chungli, Taiwan 32001 (Republic of China)

Prof. C.-H. Chen
The Genomics Research Center, Academia Sinica
Taipei, Taiwan 11529 (Republic of China)

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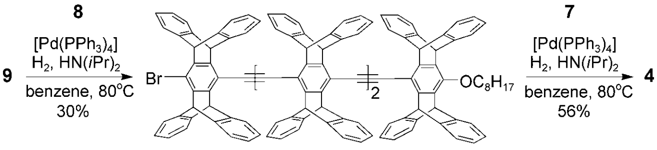
cene building blocks **7**–**9** and phenylene analogues.[12,14] For example, symmetrical double Sonogashira coupling reactions between **9** and two equivalents of **7** or **8** give rise to OPEs **3** (65%) and **5** (54%), respectively. The sequential unsymmetrical double Sonogashira reactions between **7**, **8**, and **9** under the same reaction conditions afforded **4** (Scheme 1).



***Scheme 1.*** Synthesis of OPE **4**.

Although the alternative sequence of reacting **9** first with **7** and then with **8** also led to OPE **4**, isolation of the product **4** from the remaining **8** was found to be more difficult. It should also be noted that the reported yields could be achieved only when the reaction was carried out in the presence of $H_2$.[15] Detailed synthetic schemes, procedures, and structural characterization data are provided in the Supporting Information.

The UV/Vis absorption and emission spectra of **1**–**5** in MTHF recorded at intervals of 20 K between 80 and 300 K are shown in Figure 1. The excitation wavelength ($\lambda_{ex}$) for the emission spectra is 302 nm, which is the high-energy side of the absorption band, for all cases. At this short excitation wavelength, the excited species in the cases of **1** and **2** is dominated by the twisted conformers.[12] The same situation is also expected for the cases of **3**–**5**. At 300 K, both the absorption and emission spectra are progressively red-shifted on going from **1** to **5**. This red shift is expected for a delocalized excitation and emission that arises from the increased chain length. The broader and less-structured absorption spectra for the longer OPEs reflect the increased number of conformers of varied conjugation interactions. Nevertheless, the corresponding fluorescence spectra are structured, narrow, and independent of $\lambda_{ex}$. The fluorescence 0–0 bands correspond well with the long-wavelength edge of the corresponding absorption spectra. Evidently, the torsion-relaxed planar excited state, which is not necessarily completely coplanar, dominates the observed fluorescence properties. It is interesting to note that, except for the optical transition energy, the fluorescence quantum yields ($\Phi_f = 0.71$–$0.73$),[16] lifetimes ($\tau_f = (0.7 \pm 0.1)$ ns), and rate constant ($\Phi_f/\tau_f \approx 1 \times 10^9\ s^{-1}$) are all similar for the planar conformers of **1**–**5** (Table 1). When the temperature is lowered, the absorption profile shifts to shorter wavelengths and a peak near 334 nm emerges for all cases at 80 K, at which MTHF exists as a glass.[17] This observation suggests that the conformer equilibrium shifts toward the twisted domains. Unlike the case at 300 K, the fluorescence spectra recorded at 80 K are dependent on the excitation wavelength $\lambda_{ex}$. Evidently, the excited-state torsional relaxation is no longer allowed, and conformers of distinct fluorescence wavelengths contribute to the observed spectra. In this context, it is particularly interesting to note that OPEs **1**–**5** display the same fluorescence 0–0 and 0–1 bands at 346 and 360 nm, respectively, at $\lambda_{ex} = 302$ nm.

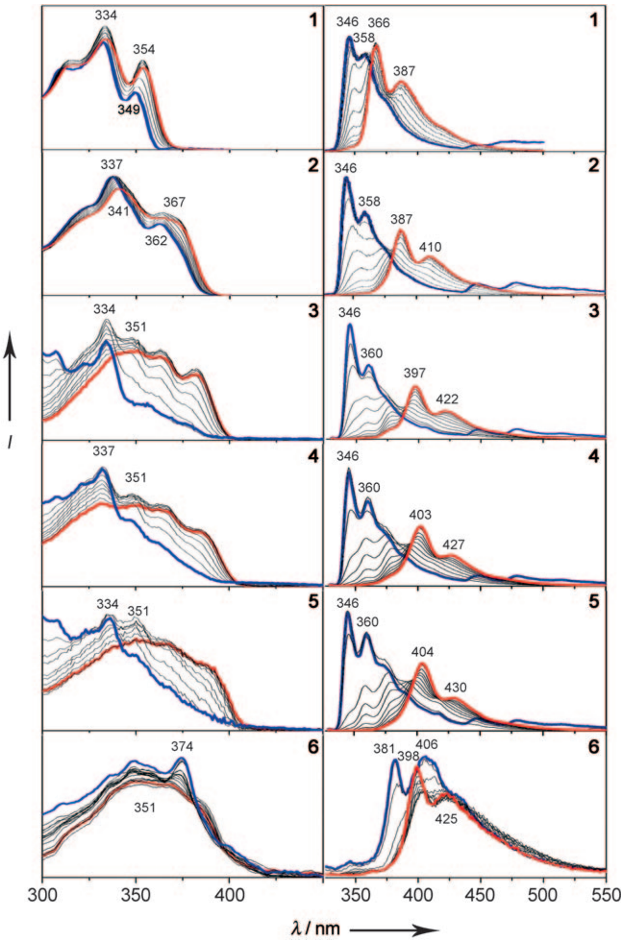


***Figure 1.*** Temperature dependence of the UV/Vis absorption (left) and emission (right) spectra ($\lambda_{ex} = 302$ nm) for **1**–**6** in MTHF at 20 K intervals between 80 K (blue) and 300 K (red).

***Table 1:*** UV/Vis absorption and emission data for **1**–**6**.[a]

| Compd | $T$ [K] | $\lambda_{abs}$ [nm][b] | $\lambda_f$ [nm][c,d] | $\tau_f$ [ns] ($\lambda_{em}$) | $\Phi_f$[e] |
|---|---|---|---|---|---|
| **1**d | 80 | 333(349) | 346(358) | 5.5 (346) | |
| | 300 | 334(354) | 366(387) | 0.7 (363) | 0.73[f] |
| **2** | 80 | 337(362) | 346(358) | 5.5 (346) | |
| | 300 | 341(367)[e] | 387(410)[e] | 0.7 (412)[e] | 0.71 |
| **3** | 80 | 334 | 346(360) | 5.5 (346) | |
| | 300 | 351 (382) | 397(422) | 0.7 (398) | 0.72 |
| **4** | 80 | 337 | 346(360) | 5.6 (346) | |
| | 300 | 351 (384) | 403(427) | 0.7 (398) | 0.73 |
| **5** | 80 | 334 | 346(360) | 5.6 (346) | |
| | 300 | 351 (385) | 404(430) | 0.7 (398) | 0.72 |
| **6** | 80 | 374 | 381(406) | 0.7 (381) | |
| | 300 | 351 (381) | 398(425) | 0.8 (400) | 0.74 |

[a] Recorded in MTHF at 300 and 80 K. [b] The second vibronic band or shoulder is given in parentheses. [c] $\lambda_{ex} = 302$ nm. [d] $\lambda_{ex} = 338$ nm. [e] Taken from Ref. [12]. [f] Taken from Ref. [13].

The fluorescence lifetimes detected at 346 nm are also the same ((5.5 ± 0.1) ns) for **1**–**5**, and the fluorescence excitation spectra (see the Supporting Information) show a reasonable match with the absorption profiles. Consequently, the fluorescence 0–0 band is blue-shifted by 20 nm for **1** on cooling from 300 to 80 K; the blue shift increases up to 58 nm for **5**.

Control experiments showed that none of the emission signal arises from the solvent.

The observation of a chain-length-independent fluorescing state for OPEs **1**–**5** at 80 K reveals that the excitation must be localized in a segment that is also the lowest-energy site (the longest π-conjugated segment) in the excited conformers, as intrachain ET is efficient (see below). This localization is possible only when the species excited at 302 nm correspond to conformers of all-twisted geometry (e.g., the TTTT form for **3**, Figure 2a), where the longest π-conjugated segment is the pentiptycenediacetylene (PDA) moiety in all cases. Indeed, the 334 nm absorption and the 346 nm fluorescence bands and the 5.5 ns fluorescence lifetime for the localized excited state resemble the spectral features of the truncated PDA model compound **10**.[13] These results not only demonstrate the concept of torsion-induced localization of excitation in conjugated oligomers but also establish the feature that OPEs with neighboring pentiptycene groups prefer to adopt a large torsion angles in the MTHF glass. Such a conformational preference is opposite to the case of OPEs with none or small substituents, which prefer the planar form at low temperatures.[13,18]

The above arguments can be further verified by the pentiptycene–phenylene hybrid OPE **6**. Firstly, the distinct preference in torsion angle for pentiptycene–pentiptycene (large torsion angle) versus pentiptycene–phenylene or phenylene–phenylene (small torsion angle) neighbors should lead to a twisted-twisted-planar-planar (TTPP) conformation for OPE **6** in MTHF at 80 K (Figure 2b), where twisted and planar again refer to large and small torsion angle, respectively. The longest planar segment in the TTPP conformer consists of three phenylene ethynylene (PE) units, which would dominate the emission at all $\lambda_{ex}$ values as long as the intrachain ET is efficient. The fluorescence 0–0 band is predicted to fall in between those of the PE trimer **8** (375 nm, see the Supporting Information) and the four-ring system **2** (387 nm) at room temperature, on the basis of chain length and substituents.[19] Indeed, the fluorescence at 346 nm is rather weak and the main fluorescence 0–0 band is located at 381 nm for **6** at 80 K (Figure 1) and is essentially independent of $\lambda_{ex}$.[20] The absorption spectrum at 80 K mirrors the corresponding excitation profile (see the Supporting Information) and displays a peak at 374 nm, which is red-shifted by 40 nm from the 334 nm band for **1**–**5**. These spectroscopic features are consistent with the predicted TTPP conformation, the concept of torsion-induced exciton localization, and the occurrence of intrachain energy hopping process. In this context, OPE **6** could be the shortest flexible CP that displays intrachain resonance ET.

A simplified summary of the excited-state dynamics and the change of excitation delocalization length for the twisted excited states of OPEs **1**–**6**, as represented by OPEs **3** and **6**, is depicted in Figure 2. At 300 K, torsional relaxation toward a planar form is rather efficient, and this process should be mainly stepwise because of the less flexible excited-state versus ground-state configuration.[11] At 80 K, torsional relaxation is inhibited and thus energy hopping either between isoenergetic sites (Figure 2a) or toward lower energy sites (Figure 2b) becomes a major event that competes with radiative and nonradiative decay processes. We can envision that the processes of torsional relaxation and energy hopping at intermediate temperatures would compete with each another before the decays occur.

The implications of our results on the photodynamics of CPs deserve further comments. The current photodynamic picture for a single molecule of CPs is in the sequence 1) a delocalized excitation over several chromophore-like subunits, 2) geometric-relaxation-assisted localization of the excitation on a single subunit, and 3) competition between intrachain resonance ET to low-energy sites and radiative or nonradiative decay processes.[21,22] The finite delocalization length of the exciton corresponds to the effective conjugation length (ECL). The ECL of CPs was estimated to be a subunit that contains around 18–22 double or triple bonds.[23] When the initial localization of excitation in step 2 is within a planar subunit longer than the ECL, the excitation essentially reaches a low-energy site and the process of torsional relaxation would be rather unimportant. In contrast, entropic torsional motions during the lifetime of chromophore could shorten the planar sub-

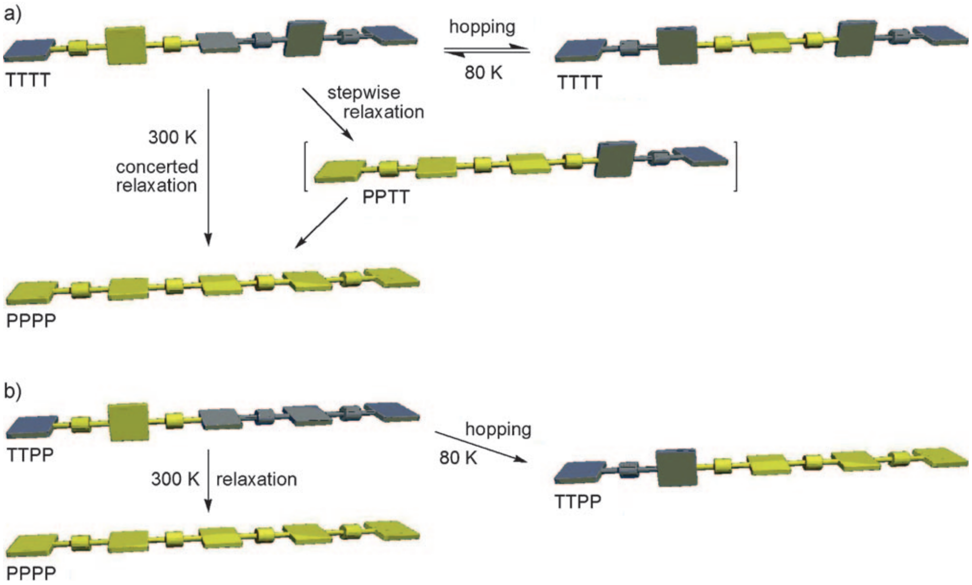


*Figure 2.* Simplified representation of the conformation-dependent excited-state dynamics for a five-ring OPE system (i.e., **3** and **6**) with allowed (300 K) and restricted (80 K) torsional relaxation: a) all-twisted (TTTT) conformer and b) a TTPP conformer. Both conformers are locally excited, and the delocalized length of the excitation is shown in yellow.

unit and slightly perturb the chromophore energy. When the initial location of excitation is in a planar subunit shorter than the ECL, torsional relaxation could occur, as in the OPEs **1**–**6** at room temperature. However, intrachain ET to neighboring subunit, particularly a lower energy site, can compete effectively. We can envision that the conformation is more static in a thin film and interchain ET becomes more important and the low-energy sites would dominate the emission, as is the case for OPEs **1**–**6** in a frozen solvent glass.

In conclusion, we have demonstrated the concept of torsion-induced localization of excitation with the chain-length-independent emission of OPEs **1**–**5** and the localized emission of OPE **6** at 80 K. This localization relies on the preference of a large torsion angle between neighboring pentiptycene groups and the restricted excited-state torsional relaxation for **1**–**6** in the MTHF glass. The ability to characterize both the twisted (at 80 K) and the planar (at 300 K) excited states of each OPE is also critical for data analysis. These results complement previous theoretical approaches and spectroscopic studies toward understanding the effect of torsion on the photophysical properties of conjugated oligomers and polymers.

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[16] We have shown that the fluorescence quantum yield $\Phi_f$ for **1** is conformer-dependent and is somewhat higher for the more planar forms (i.e., with longer $\lambda_{ex}$ values), because a nonradiative decay is accompanied with the torsional relaxation process.[13]

[17] The increased emission intensity near 300 nm for **3**–**5** at temperatures below 140 K can be attributed to light scattering of short-wavelength light scattering because of the imperfect solvent glass.

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[19] It should be noted that the five-ring OPEs **3** and **6** have a similar but different fluorescence 0–0 wavelength (397 vs. 398 nm) at 300 K (Figure 1). The presence of iptycene substituents is expected to have two opposing effects on the optical transition energy (bandgap): one is the electronic hyperconjugation effect that would lower the energy and the other is the steric effect that would reduce the degree of coplanarity of the PE backbone and thus raise the energy. The two effects cancel each other, but the steric effect appears to be slightly larger than the electronic effect on going from **6** to **3**.

[20] The fluorescence profile for **6** at 80 K is relatively broader at the high-wavelength edge compared to those for **1**–**5**. This effect could be attributed to a small degree of aggregation through π-stacking between the planar phenylene terminals of **6** at low temperatures, and is consistent with the slightly increased intensity at the long-wavelength edge of absorption spectra on cooling from 300 to 80 K (Figure 1). A similar phenomenon has been observed for the X-ray crystal structure of a model compound.[12] This phenomenon is not observed for **1**–**5** as the bulky pentiptycene groups do not allow π–π stacking of the backbones.[12]

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