

## Solid Supramolecular Architecture of a Perylene Diimide Derivative for Fluorescent Enhancement

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**Abstract:** A new *p*-phenylenevinylene-linked perylene diimide has been synthesized and self-assembled for the formation of zero-dimensional molecular aggregate structures of nanospheres and vesicles through solvent tuning. The solid-state optical properties induced by a special wavelength laser were studied and the results indicated excellent fluorescent enhancement

properties. The emission intensity of these aggregates increased with elongation of the laser irradiation time. Based on the analysis of variable-temperature <sup>1</sup>H NMR spectra, DFT calculations,

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and the single-crystal structure of the linkage group, a conformation-dependent fluorescent enhancement mechanism could be demonstrated. The mechanism is different from the fluorescent bleaching of normal solid-state fluorescent materials and offers potential applications in optical devices.

## Introduction

The field of luminescent solids has aroused much interest in recent decades<sup>[1]</sup> for their applications in light-emitting diodes<sup>[2]</sup> and field-effect transistors.<sup>[3]</sup> Many methods are well developed for tuning of their optical and electronic properties, such as photochemical isomerization by heat or light,<sup>[4]</sup> self-assembly of organic ligands and inorganic metal ions,<sup>[5]</sup> converting polymorphic materials reversibly from one form to another by external stimuli.<sup>[6]</sup> Ordered molecular assemblies can have different properties from those of their individual constituent molecules.<sup>[7]</sup> The photophysical properties of  $\pi$ -conjugated compounds in the solid state depend largely upon their molecular packing style, which can be tuned by various noncovalent forces. For example, the relative positions of adjacent molecules and directions of their dipole moments can strongly influence luminescence, exciton migration, and carrier mobility.<sup>[3a, 8]</sup> Thus to tune their properties, it is essential to understand the nature of noncovalent forces that determine molecular packing in the solid state and how they affect the photophysical proper-

ties of  $\pi$ -conjugated compounds.<sup>[6a, 9]</sup> The  $\pi$ - $\pi$  interactions in planar conjugated molecules can result in the quenching of radiative processes in the solid state and low photoluminescence efficiency, owing to the formation of H aggregates in the ground state and excimers in the excited state.<sup>[10]</sup> To reduce H aggregation, one effective way is to design nonplanar conjugated molecules to reduce  $\pi$ - $\pi$  interactions of planar conjugated molecules, such as the formation of cross dipole stacking,<sup>[8g, 11]</sup> the introduction of bulky substituents,<sup>[12]</sup> and encapsulation by clathrates.<sup>[13]</sup> Tuning the spectroscopic properties of  $\pi$ -conjugated polymers by controlling the conformations obtained from interface self-assembly was reported,<sup>[8f]</sup> but the optical properties of simple conjugated molecules, existing in the form of different conformations and spatial arrangements, have seldom been studied; this is probably due to the lack of effective measurement methods and difficulties in designing appropriate molecules. Herein, we studied the fluorescent enhancement behavior of a new *p*-phenylenevinylene-linked perylene diimide aggregate induced by laser irradiation, and a conformation-dependent mechanism was proposed based on variable-temperature <sup>1</sup>H NMR spectra, DFT calculations, and the single-crystal structure of the linkage group.

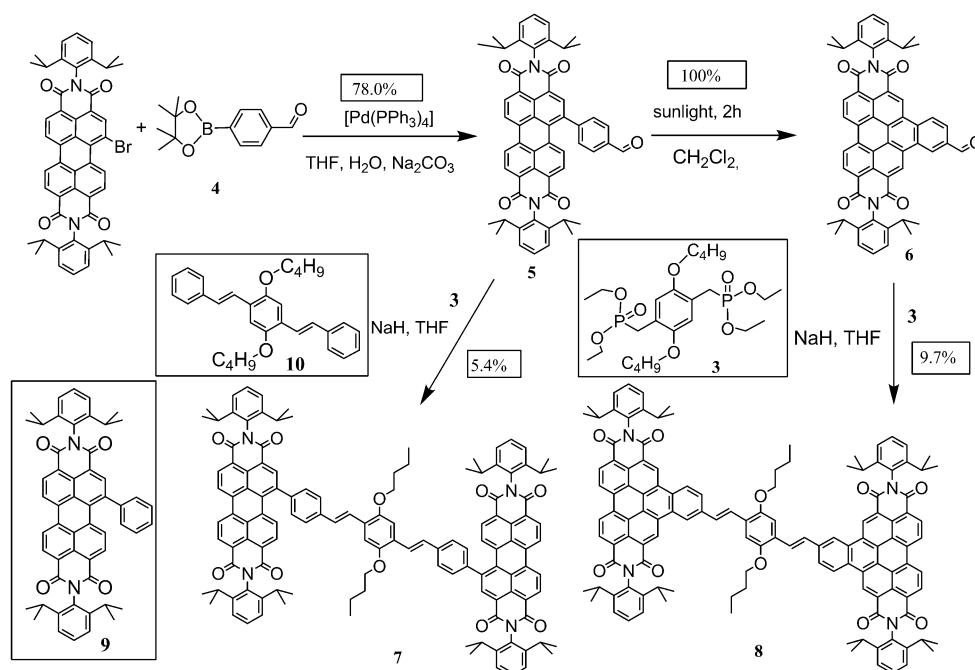
## Results and Discussion

The syntheses of compounds **7** and **8** from commercially available compounds are illustrated in Scheme 1. Compounds **3** and **4** were synthesized according to methods provided in the literature.<sup>[14]</sup> Compound **5** can be obtained in 78 % yield by the Suzuki reaction and subsequent photocyclization affords **6** in 100 % yield. When using dry THF as the solvent, in the presence of NaH, the reaction of **3** and **5** suc-

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Scheme 1. The synthetic scheme for the preparation of the compounds **7** and **8** and the molecular structures of compounds **9** and **10**. [PdCl<sub>2</sub>(dppf)]: [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II), THF: tetrahydrofuran, TBAB: tetrabutylammonium bromide.

cessfully affords compound **7**, which is an amorphous solid, in 5.4% yield after being stirred overnight at 50°C. A mixture of **3** and **6** can produce amorphous solid **8** in 9.7% yield under the same conditions. Products were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, MALDI-TOF MS, and elemental analysis. Compound **7** is soluble in dichloromethane, CHCl<sub>3</sub>, THF, and 1,1,2,2-tetrachloroethane, and microsoluble in acetone, acetonitrile, and methanol. Compound **8** is soluble in CHCl<sub>3</sub>, THF, 1,1,2,2-tetrachloroethane, but microsoluble in CH<sub>2</sub>Cl<sub>2</sub> and acetone, and insoluble in acetonitrile, methanol, *N,N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO), and toluene.

Absorption and emission spectra of these compounds in CH<sub>2</sub>Cl<sub>2</sub> at room temperature are shown in Figure 1 and their photophysical properties are listed in Table 1. The perylene core  $\pi$ - $\pi^*$  transition absorption bands ( $\epsilon_{\text{max}} = 25100 \text{ M}^{-1} \text{ cm}^{-1}$  for **7**, and  $\epsilon_{\text{max}} = 132900 \text{ M}^{-1} \text{ cm}^{-1}$  for **8**) accompanied by *p*-phenylenevinylene unit  $\pi$ - $\pi^*$  transition absorption bands can be clearly observed. Owing to steric hindrance, the *p*-phenylenevinylene moiety is nonplanar with

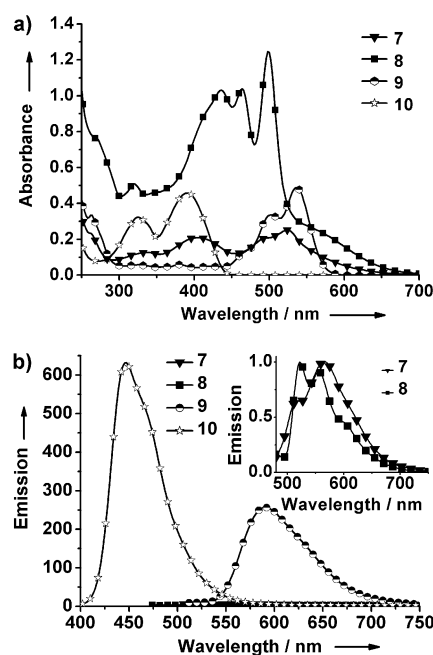


Figure 1. a) Absorption and b) emission spectra of compounds **7**, **8**, **9**, and **10** in CH<sub>2</sub>Cl<sub>2</sub> ( $2 \times 10^{-5} \text{ M}$ ) at room temperature.

respect to the perylene ring (see Figure 5 below), and acts as the electron donor in these compounds. As a result, the maximum absorption value of **7** only has a small blueshift of 3 nm relative to that of the parent compound (the unsubstituted PDI;  $\lambda_{\text{max}} = 527 \text{ nm}$ ), and the maximum absorption value of the *p*-phenylenevinylene unit only has a redshift of

#### Abstract in Chinese:

**摘要:** 合成了一种新颖的对苯撑乙烯桥联的茈二酰亚胺衍生物, 利用溶剂效应可控组装得到了零维的纳米球、纳米囊泡聚集态结构。通过特定波长的激光诱导研究了聚集态结构的光学性质, 表明其具有优良的固态荧光增强性质, 且强度随激发时间延长而增强。根据变温核磁共振谱研究以及高斯计算, 结合桥联分子对苯撑乙烯的单晶结构, 提出了一种不同于常规固体材料荧光漂白现象的构象依赖荧光增强机理。该类材料在光学器件方面存在潜在的应用。

Table 1. Photophysical and electrochemical properties of the compounds **7**, **8**, **9**, and **10**.

|           | Abs <sup>[a]</sup> $\lambda_{\max}$ [nm] | $\epsilon$ <sup>[a]</sup> [M <sup>-1</sup> cm <sup>-1</sup> ] | Fluorescence <sup>[b]</sup> $\lambda_{\max}$ [nm] | $\Phi_f$ <sup>[c]</sup> | $E_{ox}$ (V vs. SCE) <sup>[d]</sup>      | $E_{red}$ (V vs. SCE) <sup>[d]</sup>       | HOMO/LUMO [eV] <sup>[g]</sup> | $E_g$ [eV] |
|-----------|------------------------------------------|---------------------------------------------------------------|---------------------------------------------------|-------------------------|------------------------------------------|--------------------------------------------|-------------------------------|------------|
| PDI       | 527                                      | 79400                                                         | 534                                               | 1                       | 1.72 <sup>[e]</sup>                      | −0.57, <sup>[e]</sup> −0.77 <sup>[e]</sup> | −6.05/−3.90                   | 2.15       |
| <b>7</b>  | 524, 492, 403, 335                       | 25100                                                         | 574                                               | 0.008                   | 1.38, <sup>[f]</sup> 0.98 <sup>[f]</sup> | −0.61, <sup>[e]</sup> −0.83 <sup>[e]</sup> | −5.37/−3.86                   | 1.51       |
| <b>8</b>  | 498, 463, 435, 319                       | 132900                                                        | 557, 522                                          | 0.004                   | 1.44, <sup>[f]</sup> 1.11 <sup>[f]</sup> | −0.71, <sup>[e]</sup> −0.90 <sup>[e]</sup> | −5.49/−3.81                   | 1.68       |
| <b>9</b>  | 536, 502                                 | 48700                                                         | 590                                               | 0.70                    | 1.79 <sup>[f]</sup>                      | −0.58, <sup>[e]</sup> −0.79 <sup>[e]</sup> | −6.16/−3.88                   | 2.28       |
| <b>10</b> | 391, 325                                 | 45700                                                         | 447                                               |                         | 1.29, <sup>[e]</sup> 0.95 <sup>[e]</sup> |                                            | −5.39/                        |            |

[a] Measured in CH<sub>2</sub>Cl<sub>2</sub> (1.0 × 10<sup>−5</sup> M). [b] Measured in CH<sub>2</sub>Cl<sub>2</sub> (1.0 × 10<sup>−6</sup> M), upon excitation at the absorption maximum. [c] In CH<sub>2</sub>Cl<sub>2</sub>, *N,N'*-di(2,6-diisopropylphenyl)perylene-3,4:9,10-tetracarboxylic acid diimide (the unsubstituted PDI,  $\Phi_f$  = 1 in CHCl<sub>3</sub>)<sup>[15]</sup> as a standard. [d] Performed in CH<sub>2</sub>Cl<sub>2</sub> with *n*Bu<sub>4</sub>NPF<sub>6</sub> (0.05 M) as the supporting electrolyte and a standard calomel electrode (SCE) as the reference electrode. [e] Half-wave potential. [f] Peak potential. [g] HOMO and LUMO levels are obtained directly from the onset potentials measured by cyclic voltammetry, according to a method reported in the literature.<sup>[16]</sup>

12 nm from 391 to 403 nm, thus indicating that the characteristics in the absorption spectrum of compound **7** basically remain as those of the PDI and **10**. The cyclic phenyl group extends the  $\pi$  core of perylene along the short molecular axis; the absorption of **8** is blueshifted by 29 nm to 498 nm with *p*-phenylenevinylene  $\pi$ – $\pi^*$  transition absorption bands redshifted by 44 nm to 435 nm. The fluorescence quantum yields of compounds **7** and **8** are less than 0.01 based on the parent compound PDI as the standard ( $\Phi_f$  = 1 in CHCl<sub>3</sub>), indicating that they are practically nonfluorescent.

The measured redox potentials of **7** and **8** are listed in Table 1 (see Figure S1 in the Supporting Information). Compounds **7** and **8** both exhibit two irreversible one-electron oxidation peaks at 0.98 and 1.38, and 1.11 and 1.44 V, respectively. Compared with **9**, the first oxidation potential shifts negatively from 1.79 to 0.98 V for **7** and 1.11 V for **8**; this indicates that these molecules are much easier to oxidize than **9**. Compared with **10**, the first oxidation potential of **7** is positively shifted only by about 30 mV from 0.95 to 0.98 V, and that of **8** is positively shifted from 0.95 to 1.11 V (160 mV), reflecting that **7** and **8** are more difficult to oxidize than **10**. Compounds **7** and **8** both show two reversible reduction potentials. Compared with the reduction potentials of **9** (−0.58 and −0.79 V vs. SCE), the half-wave reduction potentials versus SCE ( $\nu$  = 0.1 V s<sup>−1</sup>) are −0.61 and −0.83 V for **7**, and −0.71 and −0.90 V for **8**, respectively, indicating that the reduction potentials of **7** and **8** both have a significant negative shift.

The HOMO and LUMO energy levels of these compounds and their energy gaps are also listed in Table 1. The electronic structures of the perylene derivatives are significantly different from that of the parent PDI. The  $\pi$ -electron-rich *p*-phenylenevinylene unit effectively extends the  $\pi$ -conjugation system, raising the HOMO level and leaving the LUMO level almost unchanged, thereby resulting in a smaller energy gap and making the molecules much easier to oxidize.

Variable-temperature <sup>1</sup>H NMR spectra of **7** (Figure 2b) indicated the aggregation mode between adjacent molecules. At 298 K, the singlet at  $\delta$  = 7.22 ppm is assigned to proton A (2H) of the middle benzene ring (Figure 2a). The signal from proton B (2H) of the two vinylenes split by magnetic moments of proton C into a 1:1 doublet occurs between  $\delta$  = 7.28 and 7.31 ppm, and proton C (2H) of the two vinylenes

absorbs between  $\delta$  = 7.62 and 7.65 ppm; the signal is split into two signals by magnetic moments of proton B. The four hydrogen atoms D (4H) of the two benzene rings connected with perylene give rise to a signal split by its adjacent hydrogen atom into two signals at  $\delta$  = 7.60 and 7.62 ppm, which partly overlap with the signal from proton C. From the relationship between the number of signals in the spectrum and the number of different types of hydrogen atoms in the compound, we can deduce that compound **7** is symmetric. When considering the melting and boiling points of the deuterated solvent, CD<sub>2</sub>Cl<sub>2</sub> and CDCl<sub>2</sub>CDCl<sub>2</sub> were chosen for the low (from 213 to 293 K) and high temperature (from 305 to 375 K) experiments, respectively (Figure 2b). With decreasing temperature, the signals from protons A and B both shift upfield (for example, the signal from the proton A shifts upfield from  $\delta$  = 7.21 ppm in the 293 K spectrum to  $\delta$  = 6.94 ppm in the 213 K spectrum), but the other signals shift a little or remain the same, as indicated in Figure 2b. The induced magnetic fields generated by the circulation of delocalized  $\pi$  electrons can either shield or deshield nearby protons. Whether a proton is shielded or deshielded and the extent to which shielding or deshielding occurs mainly depend on the location of the proton in the induced field.<sup>[17]</sup> When the temperature is 293 K or higher, proton A is deshielded by both the middle benzene ring and the adjacent vinylenes group (Figure 2a and b). With decreasing temperature, proton A is not only deshielded, mainly by the two intramolecular groups, but also gradually shielded weakly by other nearby molecular benzene rings and vinylenes groups, resulting in the upfield shift. The situation for proton B is similar. Compound **7** retains a symmetrical structure throughout the variable-temperature experimental processes because no signal splitting in the signal from proton A (2H) of the middle benzene ring, but the upfield shift was observed. The aggregation style of **7** can be inferred as that depicted in Figure 2c and d from the above data. The adjacent molecules of **7** aggregate through face to face  $\pi$ – $\pi$  stacking of the middle benzene ring as a center and there is an angle of about 101° between the two vinylenes (see Figure 6 below and Figure 2d).

The  $\pi$ – $\pi$ -stacking interactions of **7** induced good zero-dimensional nanostructures. Compound **7** (1.0 × 10<sup>−4</sup> M, 5  $\mu$ L) in CH<sub>2</sub>Cl<sub>2</sub> was put onto a silicon substrate with simultaneous addition of cyclohexane (5  $\mu$ L): the combined system evapo-

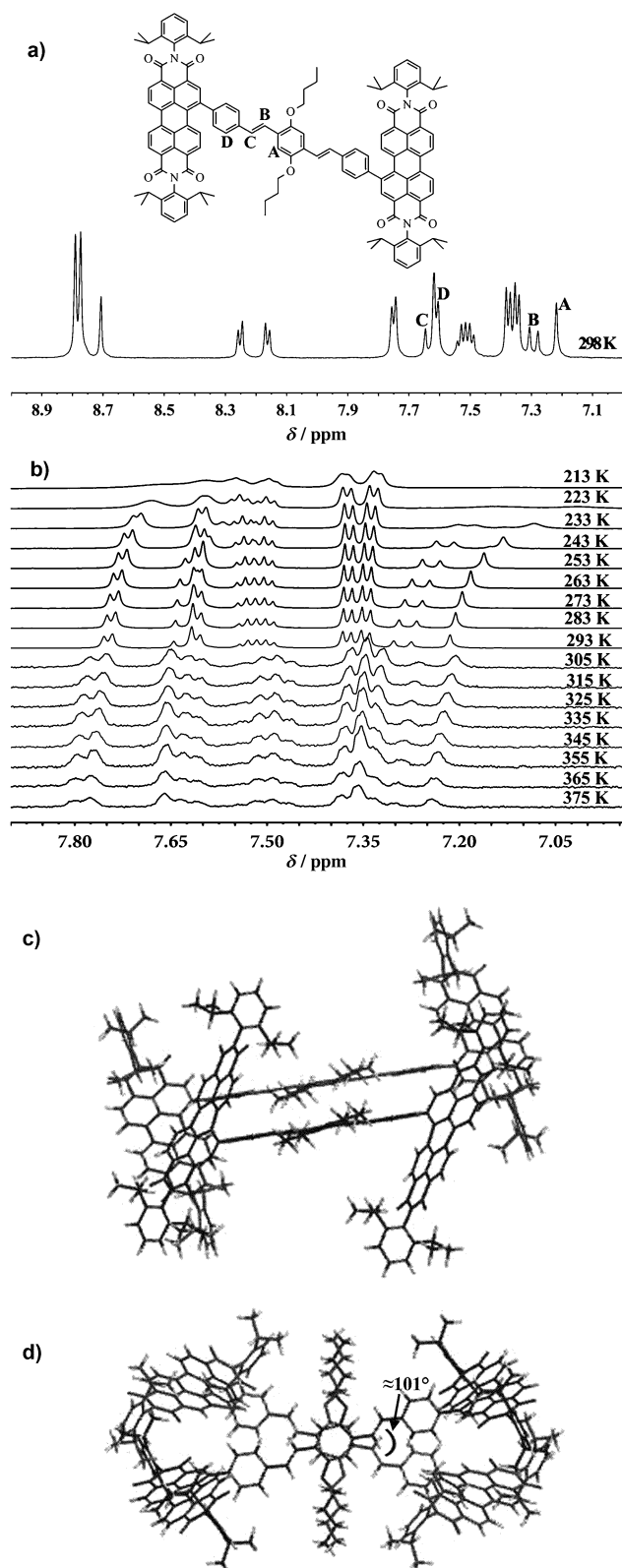


Figure 2. a) Room-temperature  $^1\text{H}$  NMR spectrum (600 MHz) of **7** in  $\text{CD}_2\text{Cl}_2$ . b) Variable-temperature  $^1\text{H}$  NMR spectra of **7** recorded at 600 MHz in  $\text{CD}_2\text{Cl}_2$  from 213 to 293 K and recorded at 300 MHz in  $\text{CDCl}_3/\text{CDCl}_2$  from 305 to 375 K. Side (c) and top views (d) of the aggregates of the most stable thermodynamic conformation of **7**.

rates completely at room temperature and is then directly used for the SEM study. Zero-dimensional nanovesicles with diameters of about 300 nm are the main morphology (Figure 3a). However, in hexane, zero-dimensional nanospheres with diameters of about 800 nm can be observed in the SEM images (Figure 3c). The presence of these nanovesicles

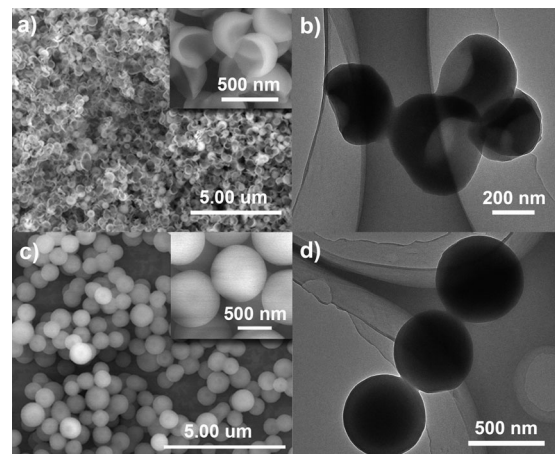


Figure 3. SEM (a and c) and TEM images (b and d) of compound **7** prepared in  $\text{CH}_2\text{Cl}_2/\text{cyclohexane}$  (1:1 v/v; a and b) or  $\text{CH}_2\text{Cl}_2/\text{hexane}$  (1:1 v/v; c and d) mixtures at room temperature.

and nanospheres were further confirmed by TEM images (Figure 3b and d). The morphological experiments clearly demonstrate that the solvent effects influence the formation of zero-dimensional nanostructures.

We further studied the optical properties of these nanoparticles with laser scanning confocal microscopy (LSCM) and found that the emission intensity increased with elongation of laser irradiation time at 515 nm. The emission band of nanospheres of **7** was observed by time-dependent fluorescent spectra with laser irradiation at 515 nm (Figure 4d). The nonfluorescent nanospheres of **7** showed an enhanced emission centered at 599 nm. The experiments related to the excitation showed that it was only the  $\pi-\pi^*$  transition absorption bands of perylene that could excite this optical behavior. These results indicate that, after self-assembly, compound **7** exhibits high selectivity to both light and wavelength. We also observed the sample prepared under the above-mentioned conditions without self-assembly because a spin-coated sample did not show these optical phenomena. In addition, other morphological self-assembled products, such as microrods and nanovesicles obtained by different self-assembly methods, can also exhibit the same phenomena of fluorescence enhancement (see Figures S2 and S3 in the Supporting Information). The MS spectrum (TOF) of the sample after laser irradiation at 515 nm still only showed a signal at  $m/z$  1844 (see the Supporting Information); this indicates the good chemical stability of **7** and indicates that the emission enhancement is not due to the photocyclization of **7** or the destruction of **7**.

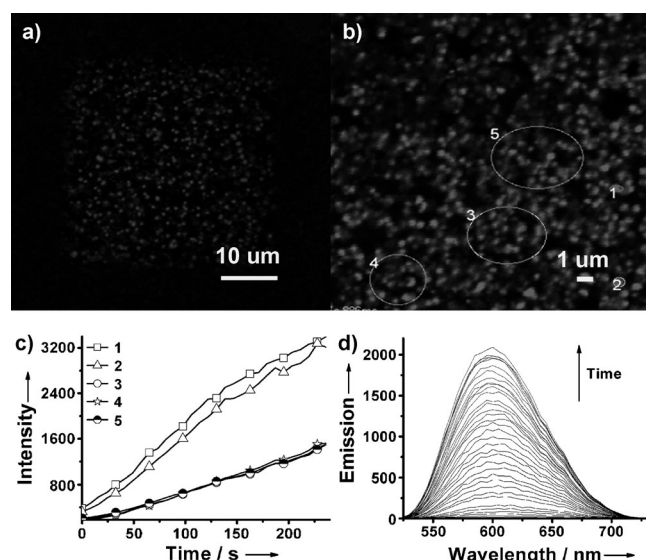


Figure 4. LSCM images after laser irradiation at 515 nm (a), time-dependent intensity plot of the fluorescence emission (b and c), and time-dependent emission spectra (d) of self-assembled spherical nanoparticles of the compound **7**. (A colored version of this figure is available in the Supporting Information.)

To gain more insight into the abnormal photophysical properties of compound **7** on the molecular level, calculations at the B3LYP/6-31G level obtained by using the Gaussian 03 program<sup>[18]</sup> for the molecular conformation of **7** were studied. The most stable thermodynamic conformation is depicted in Figure 5. The two perylene diimides are parallel, forming a dihedral angle of  $54.84^\circ$  with the *p*-phenylenevinylene unit. HOMO–LUMO analysis indicated that the electron density in the HOMO was mostly localized on the *p*-phenylenevinylene moiety and the density in the LUMO was mainly concentrated on the two PDI planes (see Figure S4 in the Supporting Information), thus reflecting that electron transfer from the *p*-phenylenevinylene moiety to the PDI planes resulted in the weak emission of PDI.

To explain the phenomena induced by the special wavelength laser reasonably, we synthesized **8** and **10** and suc-

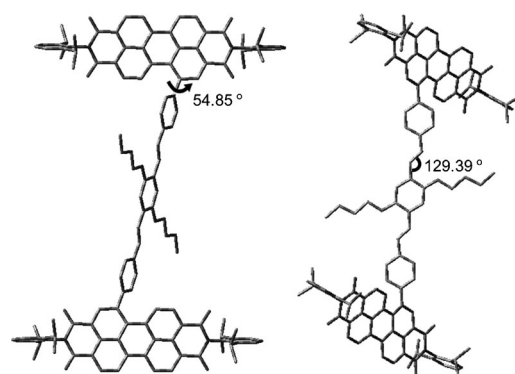


Figure 5. The most stable thermodynamic conformation of **7** obtained by using DFT calculations at the B3LYP/6-31G level.

cessfully obtained the X-ray crystal structure of **10** (see Figure S5 in the Supporting Information). The X-ray crystal structure indicates that the three benzene rings and two vinylene groups are all coplanar; this is identical to the corresponding part of the most stable thermodynamic conformation of **7** obtained by calculations (Figure 5). The control experiments for compound **8** did not reveal the same emission enhancement with laser irradiation. Based on the variable-temperature  $^1\text{H}$  NMR spectra of **7** and these control experiments, the mechanism for the phenomena could be proposed. First, owing to steric hindrance between intermolecular 2,6-diisopropylphenyl groups, and van der Waals interactions between intermolecular oxyalkyl chains, compound **7** aggregates as depicted in Figure 2c and d. There is an angle of about  $101^\circ$  between two adjacent intermolecular double bonds with the face-to-face  $\pi$ – $\pi$  stacked middle benzene ring as a center, and this style is repeated every two adjacent molecules (Figure 6). Second, under irradiation from the laser (515 nm), the molecules obtain enough energy to overcome the rotational energy barrier and rotate on its axis to and fro at the balance position, that is, the molecules change from one conformation to another. Because of steric hindrance from adjacent molecules in the self-assembled solid state, the molecule rotates to the position at which the *p*-

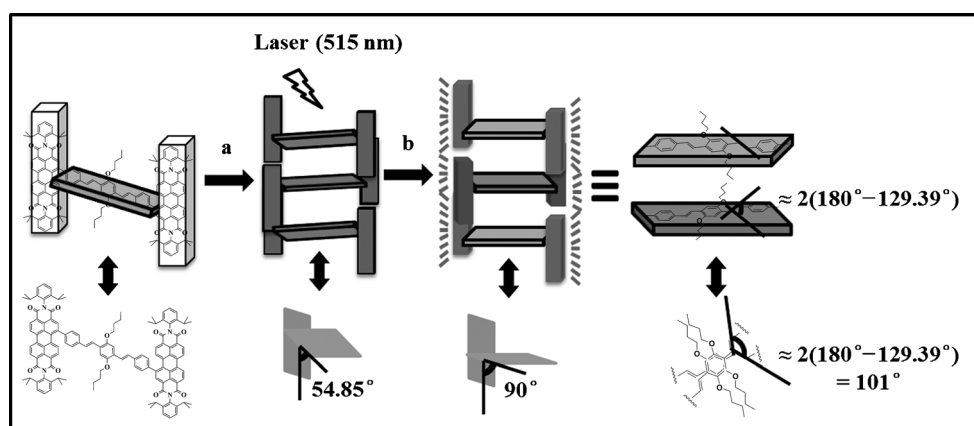


Figure 6. Proposed mechanism for the fluorescence emission enhancement of **7** after self-assembly induced by the special wavelength laser.

phenylenevinylene part is almost perpendicular to both sides of the perylene units and is stuck fast and frozen; this decreases interactions between the donor (the *p*-phenylenevinylene unit) and acceptor (the perylene group), thereby leading to the appearance of the emission of the *J*-stacked perylene diimide itself.

## Conclusion

A class of new *p*-phenylenevinylene-linked perylene diimides have been synthesized and utilized to construct zero-dimensional molecular aggregates of nanospheres and vesicles tuned by solvents. The resulting controllable organic nanoaggregate structures showed defined shapes and dimensions. The optical properties of these solid nanostructures were further studied to reveal high fluorescence in the solid state and increased emission intensity with prolonged laser irradiation. The mechanism is different from the fluorescent bleaching of normal solid-state fluorescent materials; this offers a wonderful potential application in optical devices.

## Experimental Section

### General

Chemicals and solvents were reagent grade; purchased from Aldrich, ACROS Chemical Co.; and used without further purification. *N,N'*-Di(2,6-diisopropylphenyl)-1-bromoperylene-3,4:9,10-tetracarboxylic acid diimide was synthesized according to a literature procedure.<sup>[19]</sup> Silica gel for column chromatography was purchased from JIYIDA Silica Gel Corp. in Qing Dao (200–300 mesh). <sup>1</sup>H and <sup>13</sup>C NMR spectra of the target compounds were obtained in deuterated solvents on a Bruker ARX400 spectrometer at a constant temperature of 298 K, using tetramethylsilane (TMS) as the internal standard, and chemical shifts ( $\delta$ ) are given in ppm relative to TMS. Fast-atom bombardment and HRMS was carried out on a VG ZabSpec mass spectrometer. Electronic absorption spectra were measured on a JASCO V-579 spectrophotometer. Fluorescence excitation and emission spectra were recorded by using a Hitachi F-4500 instrument at room temperature. Fluorescence quantum yields were determined by the optical dilute method with PDI in CHCl<sub>3</sub> as a reference ( $\Phi_f = 1.0$ ).

### General Method for Photocyclization

A dilute solution of compound in dichloromethane in a Schlenk flask was directly placed under sunlight and a particle of iodine was added. After the reaction was complete, the mixture was concentrated in vacuo to afford the crude product, and further purified by column chromatography. Cyclic voltammograms were measured at a scan rate of 100 mV s<sup>-1</sup>, using a glassy carbon electrode as the working electrode, Pt wire as the counter electrode, SCE as the reference electrode, and *n*Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M) in dichloromethane as the supporting electrolyte.

### Compound 5

A Schlenk flask was charged with *N,N'*-di(2,6-diisopropylphenyl)-1-bromoperylene-3,4:9,10-tetracarboxylic acid diimide (200 mg, 0.25 mmol), TBAB (40 mg, 0.12 mmol), **4** (70 mg, 0.30 mmol), THF (15 mL), and [Pd(PPh<sub>3</sub>)<sub>4</sub>] (12 mg, 0.01 mmol) was added. The mixture was stirred at 75 °C overnight. After being cooled to room temperature, the mixture was diluted with dichloromethane and washed with water and saturated NaCl (aq.). Upon drying over anhydrous Na<sub>2</sub>SO<sub>4</sub>, the organic layer was condensed in vacuo and the crude product was purified by column chromatography over silica gel, eluted with CH<sub>2</sub>Cl<sub>2</sub>, to afford **5** as a red solid (159 mg, 78.0%). M.p. 220 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 10.17 (s, 1H), 8.87–8.77 (m, 4H), 8.69 (s, 1H), 8.25 (d, *J* = 8.2 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 2H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.56–7.46 (m, 2H), 7.37 (dd, *J* = 10.2, 8.0 Hz, 4H), 2.84–2.72 (m, 4H), 1.22–1.17 ppm (m, 24H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 191.49, 163.59, 163.56, 163.39, 163.31, 148.66, 145.73, 145.70, 140.42, 136.25, 135.92, 135.50, 134.88, 134.71, 133.41, 132.05, 131.99, 131.76, 130.67, 130.51, 129.89, 129.82, 129.80, 129.70, 129.39, 128.52, 127.92, 124.25, 124.21, 123.56, 123.45, 123.25, 122.84, 122.71, 29.36, 29.28, 24.12 ppm; IR (KBr):  $\tilde{\nu}$  = 2965, 2930, 2870, 1705, 1668, 1593, 1461, 1404, 1341, 1252, 1201, 964, 816, 747, 669, 558 cm<sup>-1</sup>; HRMS (EI): *m/z* calcd for C<sub>35</sub>H<sub>46</sub>N<sub>2</sub>O<sub>5</sub>: 814.3407; found: 814.3417.

matography over silica gel, eluted with CH<sub>2</sub>Cl<sub>2</sub>, to afford **5** as a red solid (159 mg, 78.0%). M.p. 220 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 10.17 (s, 1H), 8.87–8.77 (m, 4H), 8.69 (s, 1H), 8.25 (d, *J* = 8.2 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 2H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.56–7.46 (m, 2H), 7.37 (dd, *J* = 10.2, 8.0 Hz, 4H), 2.84–2.72 (m, 4H), 1.22–1.17 ppm (m, 24H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 191.49, 163.59, 163.56, 163.39, 163.31, 148.66, 145.73, 145.70, 140.42, 136.25, 135.92, 135.50, 134.88, 134.71, 133.41, 132.05, 131.99, 131.76, 130.67, 130.51, 129.89, 129.82, 129.80, 129.70, 129.39, 128.52, 127.92, 124.25, 124.21, 123.56, 123.45, 123.25, 122.84, 122.71, 29.36, 29.28, 24.12 ppm; IR (KBr):  $\tilde{\nu}$  = 2965, 2930, 2870, 1705, 1668, 1593, 1461, 1404, 1341, 1252, 1201, 964, 816, 747, 669, 558 cm<sup>-1</sup>; HRMS (EI): *m/z* calcd for C<sub>35</sub>H<sub>46</sub>N<sub>2</sub>O<sub>5</sub>: 814.3407; found: 814.3417.

### Compound 6

Compound **5** (0.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (500 mL) was irradiated with sunlight for about 2 h; the red solution became yellow. After the solvent was removed in vacuo, the crude product was purified by column chromatography over silica gel, eluted with CH<sub>2</sub>Cl<sub>2</sub>, to give an orange solid **6** (81 mg, 100%).<sup>[20]</sup> M.p. > 300 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 10.55 (s, 1H), 10.41 (s, 1H), 10.35 (s, 1H), 9.88 (s, 1H), 9.54 (d, *J* = 8.6 Hz, 1H), 9.42 (d, *J* = 8.0 Hz, 2H), 9.21 (d, *J* = 8.0 Hz, 2H), 8.62 (d, *J* = 8.6 Hz, 1H), 7.63–7.54 (m, 2H), 7.43 (dd, *J* = 7.8, 1.4 Hz, 4H), 2.97–2.82 (m, 4H), 1.28–1.21 ppm (m, 24H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 191.82, 164.14, 163.95, 145.87, 135.95, 134.74, 134.51, 133.18, 131.08, 130.86, 130.69, 130.01, 129.54, 129.41, 128.99, 128.30, 126.93, 126.88, 125.93, 125.81, 125.31, 124.38, 124.03, 123.95, 123.73, 123.57, 122.98, 122.89, 29.50, 24.25, 24.19 ppm; IR (KBr):  $\tilde{\nu}$  = 2964, 2927, 2869, 1706, 1669, 1597, 1466, 1420, 1356, 1323, 1252, 1206, 944, 815, 747, 671, 526 cm<sup>-1</sup>; HRMS (EI): *m/z* calcd for C<sub>35</sub>H<sub>44</sub>N<sub>2</sub>O<sub>5</sub>: 812.3250; found: 812.3263.

### Compound 7

A solution of **3** (0.14 g, 0.27 mmol) and **5** (0.55 g, 0.68 mmol) in dry THF (10 mL) was added dropwise under nitrogen to a stirred suspension of NaH (38 mg, 1.6 mmol) in THF (5 mL) at 0 °C, and the mixture was heated to 50 °C overnight. Water was added to quench the reaction mixture, followed by extraction with dichloromethane. The combined organic layers were dried over sodium sulfate and concentrated. Compound **7** (27 mg, 5.4% yield) was obtained after column chromatography using dichloromethane as the eluent. M.p. > 300 °C; <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 8.78 (d, *J* = 6.9 Hz, 8H), 8.70 (s, 2H), 8.25 (d, *J* = 8.2 Hz, 2H), 8.16 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 4H), 7.62 (dd, *J* = 16.5, 8.2 Hz, 6H), 7.51 (dt, *J* = 11.5, 7.8 Hz, 4H), 7.36 (dd, *J* = 11.5, 7.8 Hz, 8H), 7.29 (d, *J* = 16.5 Hz, 2H), 7.22 (s, 2H), 4.11 (t, *J* = 6.4 Hz, 4H), 2.76 (ddt, *J* = 20.5, 13.6, 6.8 Hz, 8H), 1.92–1.84 (m, 4H), 1.59 (dd, *J* = 14.9, 7.5 Hz, 4H), 1.22–1.07 (m, 48H), 1.02 ppm (t, *J* = 7.5 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 164.14, 164.01, 163.88, 151.65, 146.47, 146.42, 142.23, 141.77, 138.88, 136.73, 135.82, 135.76, 135.47, 133.52, 131.96, 131.69, 131.46, 130.92, 130.75, 130.14, 129.94, 129.88, 129.48, 129.42, 128.90, 128.81, 128.34, 127.21, 124.93, 124.52, 124.46, 124.42, 123.61, 123.51, 122.73, 122.67, 110.91, 69.57, 31.96, 29.57, 29.49, 24.13, 19.89, 14.13 ppm; IR (KBr):  $\tilde{\nu}$  = 2961, 2927, 2867, 1705, 1666, 1591, 1463, 1405, 1340, 1249, 1199, 965, 813, 746, 667, 565 cm<sup>-1</sup>; MALDI-TOF: *m/z*: 1842.6 [C<sub>126</sub>H<sub>114</sub>N<sub>4</sub>O<sub>10</sub>]; elemental analysis calcd (%) for C<sub>126</sub>H<sub>114</sub>N<sub>4</sub>O<sub>10</sub>: C 82.06, H 6.23, N 3.04; found: C 81.92, H 6.28, N 2.95.

### Compound 8

A solution of **3** (57 mg, 0.11 mmol) and **6** (227 mg, 0.28 mmol) in dry THF (10 mL) was added dropwise under nitrogen to a stirred suspension of NaH (16 mg, 0.66 mmol) in THF (5 mL) at 0 °C, and the mixture was heated to 50 °C overnight. Water was added to quench the reaction mixture, followed by extraction with dichloromethane. The combined organic layer was dried over sodium sulfate and concentrated. Compound **8** (20 mg, 9.7% yield) was obtained after column chromatography using dichloromethane as the eluent. M.p. > 300 °C; <sup>1</sup>H NMR (353 K, 300 MHz, CDCl<sub>3</sub>/CDCl<sub>2</sub>):  $\delta$  = 10.31 (s, 2H), 10.24 (s, 2H), 9.33 (m, 8H), 9.15 (t, *J* = 8.6 Hz, 4H), 8.49 (d, *J* = 8.6 Hz, 2H), 8.03 (d, *J* = 16.4 Hz, 2H), 7.73 (d, *J* = 16.4 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 4H), 7.44 (d, *J* = 7.5 Hz, 10H), 4.29

(t,  $J = 5.0$  Hz, 4H), 2.99–2.92 (m, 8H), 2.12–1.99 (m, 4H), 1.81–1.69 (m, 4H), 1.32 (m, 48H), 1.15 ppm (t,  $J = 7.3$  Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 164.12, 163.91, 163.87, 163.80, 163.48, 151.60, 146.00, 145.92, 145.88, 145.86, 145.77, 145.74, 138.98, 138.95, 133.62, 133.58, 133.56, 133.50, 133.48, 133.42, 130.94, 130.87, 129.96, 129.88, 129.83, 128.04, 128.00, 127.98, 127.93, 127.87, 127.83, 127.76, 127.42, 126.56, 126.51, 124.53, 124.38, 124.21, 124.17, 124.14, 124.10, 122.94, 122.87, 122.80, 122.60, 122.57, 122.49, 122.37, 69.04, 31.82, 29.76, 29.67, 24.45, 19.75, 14.25$  ppm; IR (KBr):  $\tilde{\nu} = 2961, 2926, 2864, 1708, 1668, 1598, 1465, 1423, 1357, 1326, 1251, 1198, 965, 814, 747, 667, 525$   $\text{cm}^{-1}$ ; MALDI-TOF:  $m/z$ : 1862.2 [ $\text{C}_{126}\text{H}_{110}\text{N}_4\text{O}_{10} + \text{Na}^+$ ]; elemental analysis calcd (%) for  $\text{C}_{126}\text{H}_{110}\text{N}_4\text{O}_{10}$ : C 82.24, H 6.02, N 3.04; found: C 82.01, H 6.17, N 3.08.

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