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Optical Properties of Oligo(fluorene-vinylene) Functionalized Anthracene Linear Oligomers: Effect of π-extension

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The photo-physical properties of oligo(fluorene-vinylene) functionalized anthracene linear oligomers (An-OFV$_n$ (n=1−4)) have been systemically investigated through experimental and theoretical methods. The steady-state spectral measurement shows that the increasing of fluorene-vinylene (FV) group could lead to the red shift of absorption spectra and restrain the excimer formation between oligomers. Quantum chemical calculations exhibit that the energy levels of HOMO, LUMO, and the band gap gradually converge to a constant in accompany with the increasing of FV unit. Meanwhile, the electronic cloud which distributes on the branch arms, also gradually enhances and makes the absorption spectral shape of oligomers become similar to that of branch arms step by step. The time-resolved fluorescence tests exhibits that the lifetime of excimer emission would be almost invariable after the number of FV group in oligomer is ≥2. In nonlinear optical test, the two-photon photoluminescence efficiency and two-photon absorption cross-section will both gradually enhance and be close to an extremum after the number of FV unit is equal to 4. These results will provide a guideline for the design of novel photo-electronic materials.

Key words: Linear conjugated oligomer, Two-photon absorption, Fluorene-vinylene group

I. INTRODUCTION

Conjugated oligomers have attracted considerable attention in the last decade due to their remarkable opto-electronic properties. Their structural malleability allows tunable optical properties, which can be exploited for different applications. Especially, the nonlinear absorption properties of oligomers have potential applications in the fields of photodynamic therapy [1], optical storage [2], optical limiting [3], 3D micro-fabrication [4, 5] and two-photon fluorescence microscopy [6], *etc.* The development and synthesis of organic molecules with excellent two-photon optical properties have advanced significantly over the past twenty years [7, 8]. Up to now, people have realized that the two-photon optical properties of molecules mainly depend on the donor-acceptor strength, conjugation length, geometry, and nature of ground and excited states [9]. Among them, increasing π-conjugated unit in linear oligomers is one of the most effective approaches, which can effectively enhance two-photon absorption (TPA) performance and change the spectral features through modulating the distribution of frontier orbitals. Many π-conjugated units, involving pyrene, benzene, biphenyl, fluorene, dithieniothiophene, and dihydrophenathrene moieties [10−12], have been selected to synthesize the organic molecules with strong nonlinear optical properties [13, 14]. Recently, Lu *et al.* have reported a series of anthracene-based linear oligomers bearing oligo(fluorene-vinylene) arms (An-OFV$_n$ (n=1−4)) [15]. Fluorene-vinylene (FV) group acting as a π-conjugated unit and π-electron bridge is able to facilitate the delocalization of electron through expanding the π-conjugated system, and the introduction of side chains can improve the solubility of oligomers. These linear oligomers show gradual enhancing two-photon properties as the number of FV unit increases. Since reports that focus on anthracene-based linear conjugated system are limited, it is necessary to systemically understand their basic photo-physical mechanism and electronic properties.

In this work, we investigate the photo-physical properties of oligo(fluorene-vinylene) functionalized anthracene linear oligomers An-OFV$_n$ (n=1−4) (as shown in Fig.1) by experimental and theoretical methods. We detailedly study their linear and nonlinear optical properties using steady-state absorption, emission, time-correlated single-photon counting (TCSPC), two-photon fluorescence and femtosecond z-scan technique.

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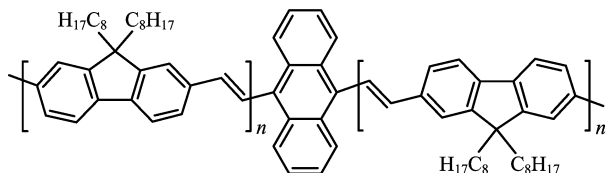
FIG. 1 Molecular structure of An-OFV$_n$ (n=1−4).

Meanwhile, we also discuss the evolution of absorption spectra with the increasing of FV unit, by resolving the electronic transition mechanism that is calculated with density functional theory (DFT). All the results lead to new design criteria for development of conjugated linear two-photon fluorescent oligomer.

II. EXPERIMENTS

A. Compounds

We prepared An-OFV$_n$ (n=1−4) toluene solutions with concentrations around 0.05 and 0.5 mmol/L for linear and nonlinear optical measurements, respectively. The samples were placed in a 2 mm thick quartz cuvette during optical measurements.

B. Optical measurements

Steady-state absorption measurements were carried out in a UV-Vis absorption spectrometer (Purkinje, TU-1810PC). One and two-photon photoluminescence (PL) measurements were achieved by using of fiber optic spectrometer (Ocean Optics, USB4000). Femtosecond Titanium:Sapphire laser (Coherent) was used as radiation source, which offers 2.2 mJ, 130 fs pulses at 800 nm with a repetition rate of 1 kHz. TPA measurements were carried out by employing the femtosecond open aperture z-scan technique, and the laser beam was modulated by means of a mechanical chopper (∼500 Hz). The laser pulses were focused onto a 2 mm thick quartz cuvette containing the sample solution with a plano-convex lens (focal length of 100 mm). The Gaussian laser beam waist ω_0 was measured to be ∼30 μm using the scanning knife-edge technique. The z-scan signal passed through a lock-in amplifier and was finally detected by PMT (Zolix, PMTH-S1-CR131A). Time-resolved PL measurements were performed on a mini-τ fluorescence spectrometer equipped with an EPL405 laser diode (Edinburgh).

C. Computational details

All calculations on compounds of An-OFV$_n$ (n=1−4) were done on the Gaussian 09 program package [19] using DFT. Becke's three-parameter functional [16] combined with Lee, Yang, and Parr's correlation functional
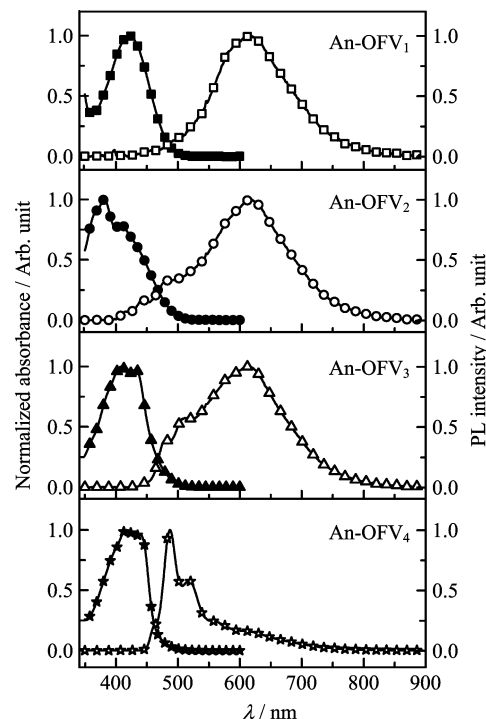
FIG. 2 Steady-state absorption (solid symbol) and photoluminescence (open symbol) spectra of An-OFV$_n$ (n=1−4).

[17] (B3LYP), along with 6-31G basis set was used. The influence of peripheral carbon chains is believed to be sufficiently small that such chains were replaced by alkyl groups in our calculations. All the geometries and electronic properties were calculated by assuming all oligomers to be isolated molecules in vacuum.

III. RESULTS AND DISCUSSION

Figure 2 shows the normalized absorption and PL spectra of An-OFV$_n$ (n=1−4) in toluene (0.05 mmol/L), and their spectral feature gradually becomes complex with the extension of branch arms. An-OFV$_1$ shows a single absorption peak at 424.5 nm. When the number of FV unit is ≥2, two absorption bands appear in the absorption spectra of oligomers and both of them red shift as the number of FV unit increases. When the number of FV unit increases to 4, the absorption peaks have already red shifted to 417.5 and 438.5 nm, respectively. Similar to the absorption spectra, the PL spectra of oligomers also become complex with increasing number of FV unit. At first, only a broad unstructured PL band exists in the emission spectrum of An-OFV$_1$, and then two little PL peaks appear after the number of FV unit increases to 2. The positions of these two peaks both red shift and their spectral shapes also become more and more clear. When the number of FV unit in branch arms increases to 4, the shapes
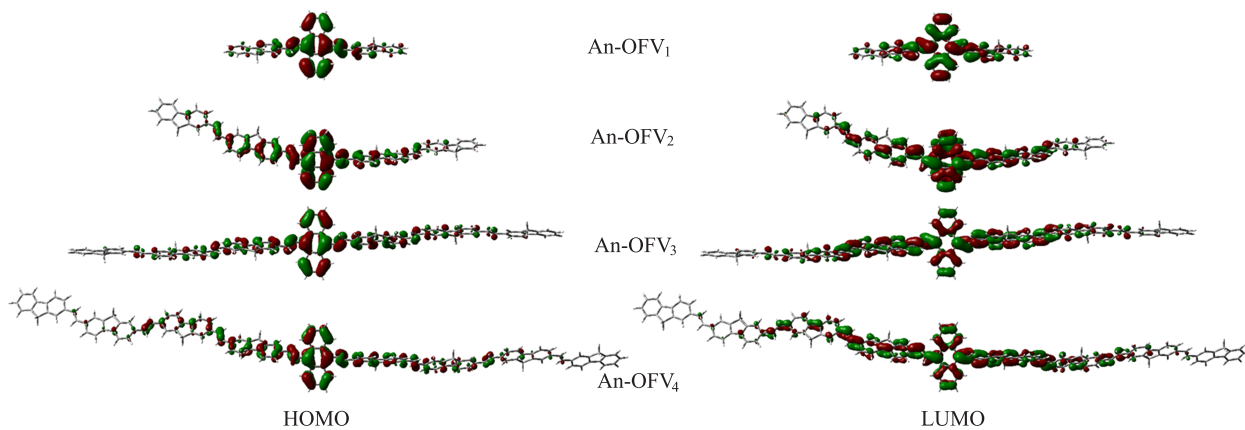
FIG. 3 HOMO and LUMO orbitals in the optimized ground state structure of An-OFV$_n$ (n=1−4).
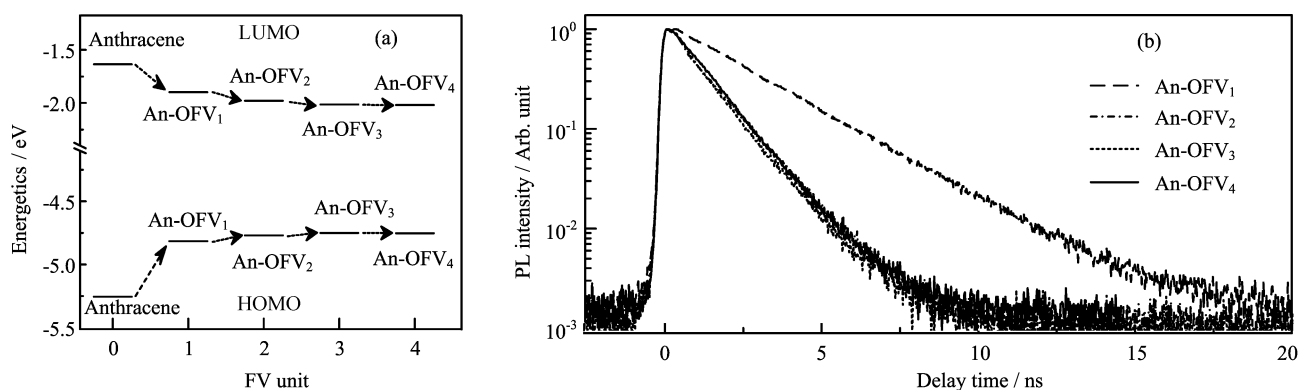

FIG. 4 (a) The energy level of HOMO and LUMO of An-OFV$_n$ (n=1−4). (b) Normalized emission kinetic traces of An-OFV$_n$ (n=1−4). Excitation wavelength is 405 nm. Detection wavelength is 600 nm.

of two PL peaks become so clear that they have been dominant in the PL spectrum of An-OFV$_4$. As previously reported, the concentration-dependent emission spectra for An-OFV$_n$ (n=1−4) show that the "excimer" was generated in An-OFV$_n$ (n=1−4) after photoexcitation and its emission band corresponds to the broad emission band at ∼615 nm, since this emission band could weaken with the decreasing of concentration [15]. As seen in Fig.2, it is noted that the position of "excimer" emission is always at ∼615 nm in PL spectra and almost independent of the variance of FV units. It is interestingly found that the emission of "excimer" gradually weakens and becomes a shoulder when 4 FV units appear in the branch arms, indicating that the yield of "excimer" is effectively restrained. Moreover, the emission spectra of oligomers are obviously narrowed and the chroma becomes much purer through increasing the FV unit in branch arms. Moreover, the generation of "excimer" depends on the concentration in solution, indicating that its generated mechanism should depend on the intermolecular interaction, which will be discussed in future using transient absorption measurement.

In an effort to understand the FV unit-dependent photo-physical properties of oligomers at the molecular level, the ground state geometries of An-OFV$_n$ (n=1−4) were optimized with the B3LYP/6-31G basis set (not shown in this work) and their corresponding frontier molecular orbitals (HOMO and LUMO) are shown in Fig.3. According to the calculated results, we found that the anthracene and the fluorene unit in An-OFV$_1$ both show a good planarity. When the FV unit gradually increases, the anthracene unit and the fluorene units still maintain planarity, exhibiting that the extension of π-conjugated system would further facilitate the π-electron delocalization. The calculated LUMO and HOMO energy levels of the oligomers are shown in Fig.4(a). One part of electronic cloud in LUMO and HOMO is localized in the anthracene moiety, suggesting that the pristine emission should be mainly attributed to the anthracene group and the corresponding spectra should appear in the blue-green region. The other part of electronic cloud in LUMO and HOMO is distributed on the FV unit with the extension of conjugated length, which indicates that the FV unit acting as a π-spacer unit could participate in the electron transition and influence the distribution of electron density over the oligomers. Moreover, the elec-
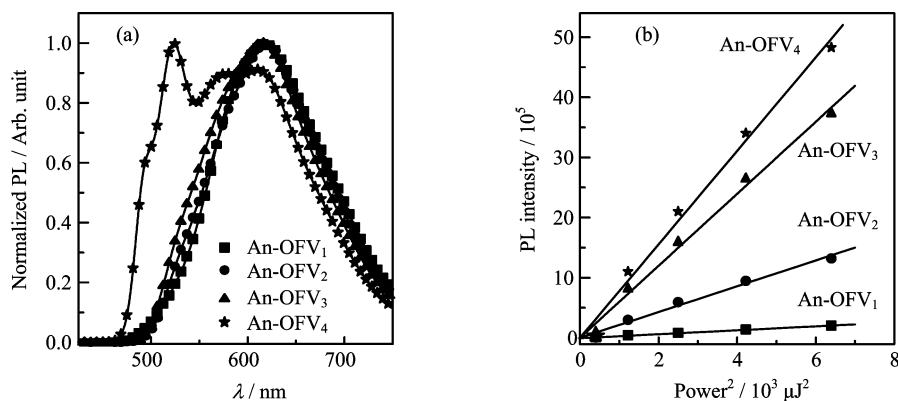
FIG. 5 (a) Two-photon PL spectra of An-OFV$_n$ (n=1−4). (b) Two-photon PL measurements as a function of laser power for An-OFV$_n$ (n=1−4).

TABLE I The photo-physical parameters obtained from experimental measurements and theoretical calculation.

	LUMO/eV	HOMO/eV	$E_g{}^a$/eV	EL^b/ns	β/(10^{-2} cm/GW)	$\sigma^{(2)}$/10^3 GM
An-OFV$_1$	−1.898	−4.815	2.917	2.54	0.2	0.17
An-OFV$_2$	−1.979	−4.769	2.790	1.10	1.3	1.07
An-OFV$_3$	−2.014	−4.750	2.735	1.03	3.5	2.89
An-OFV$_4$	−2.018	−4.751	2.734	1.16	3.9	3.22

^{a} E_g is the LUMO-HOMO energy gap.
^{b} EL is the emission lifetime.

tronic cloud distributed on the branch arms gradually enhances, and simultaneously influences the absorption spectral shape. When the number of FV unit increases to 4, the absorption spectra of An-OFV$_4$ is similar to that of E-OFV$_4$ [15], which is one of the branch arms in An-OFV$_4$. In comparison with that of isolated anthracene (3.63 eV), the calculated energy gap of An-OFV$_1$ (2.92 eV) obviously narrows due to the introduction of FV unit. As the number of FV unit increases, the HOMO, LUMO, and energy gap of An-OFV$_n$ (n=1−4) gradually converge and are expected to tend to a constant, respectively. This implies that the photo-physical parameters of oligomers may converge to an extremum after the number of FV unit becomes 4.

To further understand the basic information of excimer emission, TCSPC measurements were carried out to detect the lifetime of excimers in solution, and the lifetime values obtained by fitting the experimental data with a monoexponential function are summarized in Table I. The kinetic curves are shown in Fig.4(b), it is obvious that the emission lifetime of An-OFV$_1$ is ∼2.4 ns and longer than those (∼1.0 ns) of An-OFV$_n$ (n≥2). Moreover, the kinetic results show that the lifetime of "excimer" is almost invariable when the number of FV unit in oligomer increases more than 2, however the detailed kinetic mechanism will be discussed by using ultrafast laser spectral measurement in future.

Under the excitation of 800 nm femtosecond pulses, An-OFV$_n$ (n=1−4) in toluene solution (0.5 mmol/L)

emits intense PL, and the normalized emission spectra are shown in Fig.5(a). We measure the PL spectra with the pump energy increasing from 10 μJ to 80 μJ, and the integral PL intensities have a characteristic dependence on the square of the excitation light intensity, as seen in Fig.5(b). Combined with steady-state absorption spectra, it confirms that TPA should be responsible for the 800 nm excited PL character of all the oligomers. In comparison with PL spectra in Fig.2, we expect that the two-photon induced PL of An-OFV$_n$ (n=1−4) can also be attributed to the excimer emission and the two-photon PL (TPPL) shows a little difference in PL structure, which is mainly originated from the reabsorption effect, because of the solutions with a much higher concentration (0.5 mmol/L). In Fig.5(b), the variation of slope indicates that the TPPL yield gradually increases and will reach an extremum after the number FV unit increases to 4.

The open aperture z-scan traces of An-OFV$_n$ (n=1−4) are shown in Fig.6, which exhibits similar z-scan curves. These z-scan signatures show a minimum near the beam waist, when multi-photon absorption process happens. In order to assess the potential influence of the solvent nonlinearity, we conducted the open aperture z-scan experiment on neat toluene with the same energy as the one used on the samples. The results show that there is no effect of the laser beams on the 2 mm quartz cell and the solvent. The nonlinear absorption coefficient β can be measured by fitting the
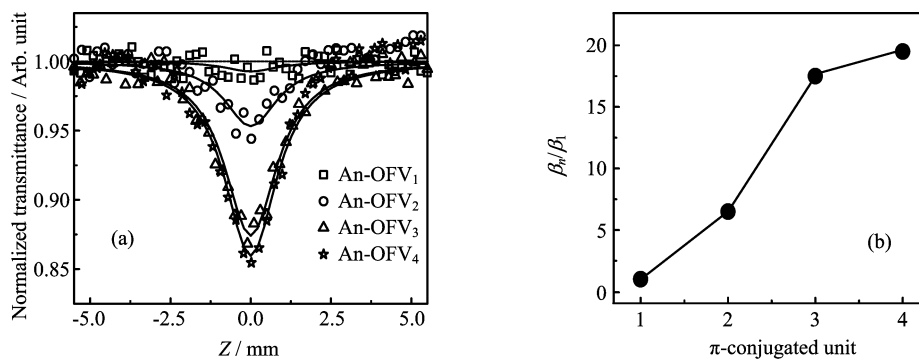
FIG. 6 (a) Open aperture z-scan signatures for An-OFV$_n$ (n=1−4) with concentration of 0.5 mmol/L. (b) The relationship between β and the number of π-conjugated unit.

experimental data with equation [18]:

$$T(z, S=1) = \frac{1}{\sqrt{\pi}q_0(z,0)} \cdot$$

$$\int_{-\infty}^{\infty} \ln[1 + q_0(z,0)e^{-\tau^2}]d\tau \quad (1)$$

$$q_0(z) = \frac{\beta I_0}{1 + z^2/z_0{}^2} \quad (2)$$

$$z_0 = \frac{1}{2}k\omega_0{}^2 \quad (3)$$

where z_0 is the Rayleigh length, k=$2\pi/\lambda$ is the wave vector, ω_0 is beam waist radius of Gaussian pulse, and I_0 is the pulse irradiance. The obtained β values are listed in Table I. The TPA cross-sections ($\sigma^{(2)}$) can be obtained through the expression

$$\sigma^{(2)} = \frac{h\nu\beta}{N} \quad (4)$$

N is the number of molecules per cm^3, $h\nu$ is the photon energy, and $\sigma^{(2)}$ is usually expressed in Göppert-Mayer units (GM), 1 GM=10^{-50} cm^{4}s/(molecule photon). The values obtained for the TPA cross-sections are also summarized in Table I.

Figure 6(b) shows the relationship between β and the number of conjugated unit. The TPA cross-section $\sigma^{(2)}$ of An-OFV$_n$ (n=1−4) rises from 0.17×10^3 GM to 3.22×10^3 GM, and the amplitude of enhancement gradually decreases, indicating that the TPA of anthracene-based linear conjugated oligomer bearing FV unit may converge to an extremum, and the increasing of FV unit could not further improve the TPA cross-section efficiently. In a word, we should admit that the oligo(fluorene-vinylene) unit acting as a key element could enhance the TPA cross-section of linear anthracene-based oligomers, meanwhile it could also restrain the generation of "excimer" and improve the photo-physical properties of anthracene-based linear oligomers.

IV. CONCLUSION

We reported the experimental and theoretical investigation on the photo-physical properties of the oligo(fluorene-vinylene) functionalized anthracene-based oligomers. The results show that the contribution of FV units is gradually dominant in the photo-physical properties of oligomers with the extension of conjugated system. Moreover, the nonlinear optical properties such as TPPL efficiency and TPA cross-section gradually improve and tend to a constant as the number of FV unit increases. The chemical calculation surveys this phenomenon through electronic transition mechanism and points out that the redistribution of electronic cloud with the extension of conjugated system should be responsible for the change of optical properties of oligomers. From a technological point of view, the results presented in this study can guide the development of two-photon fluorescent materials and their derivatives in the visible and near-infrared region.

V. ACKNOWLEDGMENTS

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