Effect of Bridging Position on the Two-Photon Polymerization Initiating Efficiencies of Novel Coumarin/Benzylidene Cyclopentanone Dyes

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One- and two-photon photophysical and photochemical properties of dyes **3-DAC** and **4-DAC** containing coumarin and benzylidene cyclopentanone moieties were studied. Their ground state configurations were optimized using both Hartree—Fock and density functional theory (B3LYP functional) methods, and excited-state properties were calculated using time-dependent density functional theory. These two dyes share the same formula and possess similar structures, except for different bridging positions between the benzylidene cyclopentanone and coumarin moieties. The bridging position was found to have a significant effect on the electronic structure and photophysical and photochemical properties of the dyes. **3-DAC** shows higher conjugation and is more planar than **4-DAC**, and it exhibits a larger TPA cross section. In contrast, **4-DAC** has a twisted conformation, exhibits a lower electron transfer free energy with initiator and shows higher sensitizing efficiencies in one-photon polymerization. Furthermore, the application potential of **3-DAC** and **4-DAC** in two-photon polymerization (TPP) was studied. Both dyes could be used directly as initiators in TPP. The TPP threshold energies of the corresponding resins were as low as the best reported results. High-resolution 2D and 3D nanopatterns containing low amounts of small molecule residue were successfully fabricated by TPP, demonstrating the extensive application prospects of these dyes in the fabrication of micromachines, microsensor arrays and biomedical devices.

Introduction

Two-photon polymerization (TPP) has attracted much attention in recent years as a powerful tool for realizing high-density optical data storage^{1,2} and three-dimensional microfabrication of functional devices.^{3–5} To improve the performance of TPP, initiators with large two-photon absorption (TPA) cross sections and high initiating efficiencies are required.

Coumarin is a robust chromophore that is used in a broad range of applications such as laser dyes,⁶⁻⁸ fluorescent probes,^{9,10} and photosensitizers.¹¹⁻¹³ Our research focuses on its application as photosensitizer in one-photon polymerization (OPP)^{14,15} and TPP.^{16–19} Because the coumarin ring mainly absorbs in the UV region, usually a conjugated group is introduced onto the coumarin ring to extend its absorption into the visible region for obtaining high performance photosensitizers.^{14,16,17} We have shown that both 3-substituted¹⁸ and 4-substituted¹⁹ coumarin derivatives exhibit high sensitizing efficiency. Such compounds also exhibit large TPA cross sections for their strong excited state charge transfer characteristics. However, because their substituents at the 7-position are different, the effect of the bridging position on the properties of these compounds cannot be directly studied by comparing these reported compounds. In this study, a novel coumarin derivative containing a benzylidene cyclopentanone substituent at the 4 position of the coumarin ring (4-DAC) was synthesized based on a reported compound **3-DAC**¹⁸ (shown in Figure 1). These two dyes have the same formula and similar structures, except that the bridging positions



Figure 1. Chemical structures of 3-DAC and 4-DAC.

between the benzylidene cyclopentanone and coumarin moieties differ. Their photophysical, photochemical, and electrochemical properties were studied to understand the influence of bridging position on the properties of coumarin dyes. Furthermore, the ground state configurations and electronic spectra of both **3-DAC** and **4-DAC** were calculated under optimized conditions using quantum chemical calculation methods. The structure—property relationships of **3-DAC** and **4-DAC** were further revealed by considering both the experimental data and theoretical calculations.

Experimental Section

Materials. 7-Diethylamino-4-methylcoumarin (Coumarin 1) and 3-mercapto-4-methyl-1,2,4-triazole (MMT) were from Avocado. Tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) (Acros Organics) was recrystallized before use. 2-[4-

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(Dimethylamino)-benzylidene]-cyclopentanone (DMA) and **3-DAC** were prepared according to literature procedures.^{14,18} 4-Dimethyldiphenyliodonium hexafluorophosphate (Omnicat 820) was from TH-UNIS Insight Co. Ltd. 2-Phenoxyethyl acrylate (SR339), pentaerythritol triacrylate (SR444), and epoxy acrylate (CN124A80) were from Sartomer Co. Ltd. and were used as received. *o*-Cl-Hexaarylbisimidazole (HABI) was from Tokyo Kasei Kogyo Co. Ltd. SeO₂ was from Sinopharm Chemical Reagent Co. Ltd. Fluorescein and other A.R. grade reagents were from Beijing Chemical Reagent Company and were used after purification by common methods.

7-Diethylamino-4-formylcoumarin. Coumarin 1 (4.62 g) and SeO₂ (3.3 g) were dissolved in xylene (120 mL). The solution was protected with dry N₂ and heated to reflux for 12 h. The mixture was filtered while hot to remove selenium, and then the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (CH₂Cl₂/ petroleum ether 10:1) and recrystallized (from CHCl₃/hexane) to give dark red needles (40%). ¹H NMR (400 MHz, CDCl₃) δ : 1.22 (t, *J* 7.1 Hz, 6 H), 3.43 (q, *J* 7.1 Hz, 4 H), 6.45 (s, 1 H), 6.53 (s, 1 H), 6.63 (s, *J* 9.2 Hz 1 H), 8.30 (d, *J* 9.2 Hz, 1 H), 10.03 (s, 1 H).

4-DAC. 7-Diethylamino-4-formylcoumarin (0.37 g, 15 mmol) and DMA (0.36 g, 16.5 mmol) were dissolved in toluene (35 mL) and protected under a dry N₂ atmosphere. The mixture was heated to reflux and then toluene-*p*-sulfonic acid (0.06 g) was added. The mixture was stirred under refluxed for 30 h. After cooling to room temperature, pyridine (4 drops) was added to neutralize the mixture. The volatile components were removed by distillation under reduced pressure. The crude product was purified by column chromatography on silica gel (CH₂Cl₂/ petroleum ether 9:1) to give 0.33 g **4-DAC** (50%). ¹H NMR (400 MHz, CDCl₃) δ : 1.22 (t, *J* 7.1 Hz, 6 H), 3.07 (s, 10 H), 3.43 (q, *J* 7.1 Hz 4 H), 6.16 (s, 1 H), 6.55 (s, 1 H), 6.61 (d, *J* 8.4 Hz, 1 H), 6.78 (d, *J* 6.5 Hz, 2 H), 7.55 (d, *J* 8.9 Hz, 3 H), 7.63 (d, *J* 7.3 Hz, 2 H). HRMS (ESI): Anal. calcd. For C₂₈H₃₁N₂O₃ [M+H]⁺: 443.23292. Found: 443.23259.

Characterization Methods. UV-vis absorption spectra were measured on a Jasco V-530 spectrophotometer. One-photon fluorescence and phosphorescence spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer. FT-IR spectra were obtained on a Varian Excalibur HE 3100 spectrophotometer. ¹H NMR spectra were obtained on a Bruker DPX400 spectrometer. Mass spectra were obtained on a Bruker Apex IV FT mass spectrometer. The fluorescence lifetime was measured using time-correlated single-photon counting technique with a gated hydrogen discharge lamp as excitation source (Edinburgh nF9000). TPP fabricated microstructures were characterized by scanning electron microscopy (SEM, Hitachi S-4300FEGd).

The solvatochromic effects of the compounds were explored in a series of different acetonitrile-toluene solutions at a concentration of 10^{-5} M. The polarity of the solvent was represented by the solvent polarity functions $f(\varepsilon, n)$ and g(n), which were calculated from the refractive index (*n*) and dielectric constant (ε) of the solvent using eqs 1 and 2. Based on quantum mechanical perturbation theory, the equations

$$\tilde{\nu}_{a} - \tilde{\nu}_{f} = m_{1} f(\varepsilon, n) + \text{const}$$
 (1)

$$\tilde{\nu}_{a} + \tilde{\nu}_{f} = -m_{2}[f(\varepsilon, n) + 2g(n)] + \text{const}$$
 (2)

were obtained. Here, $\tilde{\nu}$ is the wavenumber, the subscript "a" refers to absorption and the subscript "f" refers to fluorescence, the

parameters m_1 and m_2 can be determined by fitting $\tilde{\nu}_a - \tilde{\nu}_f$ versus $f(\varepsilon, n)$ and $\tilde{\nu}_a + \tilde{\nu}_f$ versus $f(\varepsilon, n) + 2g(n)$, respectively.^{20–22}

$$f(\varepsilon, n) = \frac{2n^2 + 1}{n^2 + 2} \left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right]$$
(3)

$$g(n) = \frac{3}{2} \left[\frac{n^4 - 1}{(n^2 + 2)^2} \right]$$
(4)

Assuming that the ground and excited states are parallel, their dipole moments are expressed by eqs 5 and 6. Here, μ_g is the ground state dipole moment, μ_e is the excited-state dipole moment, and *a* is the Onsager radius of the solute, in which it is assumed that the solute is in the shape of a sphere. The volume of the solute could be calculated with the Gaussian 03 package, using most of the calculation methods and basis sets, and thus the radii *a* is very easily ready from such calculation.

$$\mu_{\rm g} = \frac{m_2 - m_1}{2} \left[\frac{hca_3}{2m_1} \right]^{1/2} \tag{5}$$

$$\mu_{\rm e} = \frac{m_2 + m_1}{2} \left[\frac{hca_3}{2m_1} \right]^{1/2} \tag{6}$$

The fluorescence quantum yields of **4-DAC** in chloroform were determined by using fluorescein (in 0.1 M aqueous NaOH) as a standard ($\Phi_r = 0.9$); refractive index correction was performed.²³

TPA cross sections (δ) of the compounds in chloroform (2 × 10⁻⁴ M) were determined using the two-photon-excited fluorescence (TPEF) technique with femtosecond laser pulses following the experimental protocol described in detail by Xu and Webb.²⁴ The excitation light sources were a mode-locked Tsunami Ti:sapphire laser (720–880 nm, 80 MHz, <130 fs). A solution of fluorescein (10⁻⁴ M) in 0.1 M aqueous NaOH was used as the reference. To avoid any contribution from other photophysical/photochemical processes, the intensity of the input pulses were adjusted to ensure a quadratic dependence of the fluorescence intensity versus excitation pulse energy. δ was calculated by the following equation:

$$\delta = \frac{S_{\rm s} \Phi_{\rm r} \varphi_{\rm r} c_{\rm r}}{S_{\rm r} \Phi_{\rm s} \varphi_{\rm s} c_{\rm s}} \delta_{\rm r} \tag{7}$$

Here the subscripts "r" and "s" stand for the reference and sample, respectively; S is the integrated area of the TPEF; Φ is the quantum yield; φ is the overall fluorescence collection efficiency of the experimental apparatus; and c is the concentration.

The oxidation potentials of **3-DAC** and **4-DAC** were measured by cyclic voltammetry (CV) in acetonitrile using Ag/AgCl as a reference electrode, a 3 mm diameter Pt working electrode, and a Pt counter electrode. 0.1 M TBAPF₆ was the supporting electrolyte, and the compounds were dissolved in reagent grade acetonitrile with a concentration of 0.5 mmol/L. The solutions were protected with N₂ and scanned at a rate of 100 mV/s. The free energy of electron transfer (ΔG_{et}) from the dye to the initiator was calculated using the Rehm–Weller equation (eq 6).

$$\Delta G_{\rm et}(\rm kcal\ mol^{-1}) = 23.06(E_{\rm ox} - E_{\rm red} - e_{\rm o}^2/a\epsilon - E^*) \quad (8)$$

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Here, $e_o^{2/a\epsilon}$ is the energy obtained when two free ions reach distance *a* in the solvent with a dielectric constant of ϵ (0.06 eV in acetonitrile).²⁵

The sensitizing efficiencies of **3-DAC** and **4-DAC** were explored by a photobleaching experiment and OPP. The irradiation source was a 473 nm laser. The intensity of irradiation was 22 mW/cm². The other experiment conditions used for OPP were same as we reported previously.¹⁴ Compounds **3-DAC** and **4-DAC** were used as sensitizers; Omnicat 820 was used as a co-initiator.

The same mixed monomers were used in TPP experiments with **3-DAC** and **4-DAC** as sensitizer and initiator, respectively. The laser (Tsunami Ti:sapphire, 780 nm, 80 MHz, 80 fs) was tightly focused into the sample using an oil-immersion objective lens ($100 \times$, NA = 1.4, Olympus). The sample was fixed on a *xyz*-step motorized stage controlled by a computer. After laser fabrication, the unpolymerized resin was washed out using acetone. The obtained microstructures were characterized by SEM.

Calculation Methods. The electronic structure of coumarin derivatives have long been investigated theoretically by semiempirical,^{26,27} ab initio and density functional theory (DFT) methods.^{28,29} In 2002, Cave et al.^{30,31} performed a detailed theoretical study on several coumarins using different electronic structure methods and concluded that time-dependent density functional theory (TD-DFT) was a powerful method for predicting the spectroscopy of 7-aminocoumarins. More recently, the electronic spectra of a series of coumarins^{32–35} have been studied using TD-DFT and the calculated results are in good agreement with various experimental measurements.

In this work, the quantum chemical calculations were carried out using the Gaussian 03 program package.³⁶ The ground-state geometries of 3-DAC and 4-DAC, both in gas phase and solution condition, were obtained from full optimizations using the Hartree-Fock (HF) and DFT (B3LYP functional³⁷) methods with the 6-31+G(d) and 6-31G(d) basis sets, respectively. The effects of solvent were considered using the polarized continuum model (PCM)³⁸⁻⁴⁰ and default UA0 cavity, in which the solvents acetonitrile, chloroform, and toluene were employed for simulating real experimental conditions. In the GAUSSIAN program, the PCM model is performed with self-consistent reaction field (SCRF); therefore, our calculation could be denoted as B3LYP-SCRF. On the basis of optimized configurations for the ground state, TD-DFT calculations were performed using the B3LYP functional (TD-B3LYP-SCRF) within the adiabatic approximation to predict the excitation energies. The oscillator strengths (F) of the transitions and the ground to excited state transition electric dipole moments ($\Delta \mu$) were also calculated by the same method, which are very helpful in assigning the calculated electronic transitions to the experimental absorption bands.

Results and Discussion

Photophysical Properties. Absorption and emission spectra of 3-DAC and 4-DAC are shown in Figure 2. Their corresponding photophysical data are listed in Table 1. The absorption maxima of 3-DAC is significantly red-shifted and its molar absorption coefficient is larger than that of 4-DAC, which suggests that 3-DAC exhibits increased conjugation over 4-DAC. The larger Stoke's shift of 4-DAC compared with that of 3-DAC indicates a larger change in geometry between its ground state and first excited singlet state. On the other hand, the shift between the phosphorescent and fluorescent peaks of 4-DAC is much smaller than that of 3-DAC, indicating that the change in geometry between the first excited singlet-state



Figure 2. Normalized absorption and emission spectra of **3-DAC** and **4-DAC** in chloroform (phosphorescence spectra were measured in 2-methyl-tetrahydrofuran at 77 K).

and triplet-state of **4-DAC** is comparatively small. Correspondingly, the probability of this transition may be high so the triplet quantum yield of **4-DAC** is probably larger than that of **3-DAC**.

Solvatochromism. The absorption and emission maxima of the compounds in a range of toluene/acetonitrile mixtures with different polarities are listed in Table 2. The absorption peaks of 3-DAC and 4-DAC show no significant shift while their emission spectra exhibit large red shifts as the solvent polarity increases. This implies that the polarity of their excited states is much larger than that of their ground states. Figure 3 shows the peak shifts (in cm⁻¹) of $\tilde{v}_a - \tilde{v}_f$ and $\tilde{v}_a + \tilde{v}_f$ for all of the compounds versus the polarity functions $f(\epsilon, n)$ and $f(\epsilon, n)$ + 2g(n). Excellent linear relationships are found for compound 3-DAC, but for 4-DAC the emission spectra is too sensitive to the solvents. From Table 2, one can observe that when the volume percentage of acetonitrile in toluene is changed from 9 to 13%, the emission peaks of 4-DAC will be red-shifted dramatically, indicating that the data lower than 13% are much apart from the line obtained from the data above 13% volume percentage of acetonitrile in toluene (shown in Figure 3a). Therefore, we have omitted these points for calculating the m_1 and the dipole moment of 4-DAC. On the basis of eqs 3-6(refer to the Experimental section), we calculated the μ_{g} and μ_{e} of 3-DAC and 4-DAC (listed in Table 3). Both compounds show a large change of dipole moment ($\Delta \mu = \mu_e - \mu_g$) between the ground state and the first excited singlet state, which confirms the large intramolecular charge transfer ability of their excited states.

Two-Photon Absorption. The two-photon fluorescence excitation spectra of **3-DAC** and **4-DAC** were measured over a broad range of 720–880 nm, and the results are shown in Figure 4. It is obvious that the TPA cross-section of **3-DAC** is much larger than that of **4-DAC**, which means that increase the degree of conjugation could enhance the stability of the excited state and in turn increase the ratio of the transition that enlarges the TPA cross-section. Also, the two-photon excitation peak wavelengths (δ_{max}) of **3-DAC** and **4-DAC** show a significant blue-shift compared to the double wavelength of their linear absorption peaks. This suggests that the TPA in these compounds might correspond to the S0–S2 transition.

Electrochemical Properties. Typical cyclic voltammograms (CVs) of **3-DAC** and **4-DAC** are shown in Figure 5. The scans show irreversible oxidation peaks in the 0.0–1.8 V (vs Ag/AgCl) range. The peak shapes of **3-DAC** and **4-DAC** are quite similar; however, the oxidative potential of **3-DAC** is smaller than that of **4-DAC**. A reduction potential for Omincat 820 of

 $\frac{\tau_{\rm t}~(\rm ns)}{0.77}$

0.75

TABLE 1: One- and Two-Photon Optical Properties of 3-DAC and 4-DAC in Chloroform ^a										
compound	λ^a_{max} (nm)	$\epsilon_{max}~(10^4~M^{-1}cm^{-1})$	$\lambda_{max}^{\rm fl} \ (nm)$	λ_{max}^{ph} (nm)	$\Delta v_{\rm ss}~(10^3{\rm cm}^{-1})$	Φ	$k_{\rm f} \; (10^8 \; {\rm s}^{-1})$	$k_{\rm r} \; (10^8 \; {\rm s}^{-1})$	$\delta_{\max}~(\mathrm{GM})$	$\delta_{\rm avg}~({\rm GM})$
3-DAC	500.0	6.6	564.0	700	2.27	0.09	0.67	12.7	769	300
4-DAC	471.0	4.2	617.4	659	5.03	0.05	1.17	11.8	199	107

 ${}^{a}\lambda_{\max}^{a}, \lambda_{\max}^{d}, \lambda_{\max}^{a}$, and λ_{\max}^{ph} are the absorption maxima, fluorescence maxima and phosphorescent maxima, respectively; ε_{\max} is the molar absorption coefficient; Δv_{ss} is the Stokes shift; Φ is the fluorescence quantum yield; k_{f} and k_{r} are the radiative and nonradiative rate constants; δ is the two-photon absorption cross section; τ_{t} is the fluorescence lifetime.

TABLE 2: Absorption and Emission Maxima of 3-DAC and 4-DAC in Toluene/Acetonitrile Mixtures ($[dye] = 1 \times 10^{-5} \text{ M}$)

solvent ^a (%)	0	2	5	9	13	16	20	40	60	80	100
λ_{\max}^{a} (nm)	485.5	488.5	489.5	492.5	494.0	494.5	495.5	497.5	497.5	497.0	495.0
					3-DAC						
$\lambda_{\rm max}^{\rm fl}$ (nm)	520.0	526.4	534.6	546.4	551.2	558.8	562.0	567.0	574.6	581.6	579.0
λ_{\max}^{a} (nm)	452.5	454.0	456	457.5	457.5	459.5	460.0	462.0	460.0	461.0	457.5
4-DAC											
$\lambda_{\max}^{\mathrm{fl}}$ (nm)	481.0	482.0	492.7	505.6	525.3	532.4	538.0	544.2	549.0	551.0	557.0

^a The numbers denote the volume percentage of acetonitrile in toluene.



Figure 3. Plot of (a) $\tilde{v}_a - \tilde{v}_f (\text{cm}^{-1}) \text{ vs } f(\varepsilon, n)$ and (b) $\tilde{v}_a + \tilde{v}_f (\text{cm}^{-1}) \text{ vs } f(\varepsilon, n) + 2g(n)$ for **3-DAC** and **4-DAC** in a mixture of solvents.

-0.5 V was obtained by scanning in the range -1.8 to 0 V (vs Ag/AgCl). Table 4 shows the resulting redox potentials and free energy of electron transfer (ΔG_{et}) from the dyes to the initiator calculated from the Rehm–Weller equation (see eq 8 in the Experimental section). The ΔG_{et} of both sensitize-initiating systems are much smaller than -10 kcal/mol, indicating that electron transfer from the dyes to the initiator occurs readily after excitation of the dye.⁴¹ Though the oxidative potential of **3-DAC** is smaller than that of **3-DAC**, so the ΔG_{et} of **4-DAC** is

smaller than **3-DAC**. This indicates that electron transfer from **4-DAC** to Omnicat 820 is more facile than from **3-DAC** to Omnicat 820. The photosensitizing efficiency of **4-DAC** may be higher than that of **3-DAC**.

Photobleaching and One-Photon Polymerization. The primary photoreaction between the dyes and the initiator Omnicat 820 was studied using a common photobleaching experiment. When the dye/Omnicat 820 system was exposed to a 473 nm laser, the dye was oxidized and its absorption peak would decrease with irradiation time because of photoinduced electron transfer from the dye to Omnicat 820. A kinetic study of the photoreaction was carried out by monitoring the relative change in the optical density (OD) at the absorption maxima of the dye over the irradiation time. It was found that the photobleaching rate Rb (Rb = (OD₀ – OD)/(OD₀t)) of **4-DAC** is faster than that of **3-DAC** with Omnicat 820 (shown in Figure 6a).

The initiating efficiency of the dye/Omnicat 820 system was further investigated by OPP. Through monitoring the relative change in the absorption of the double bond of acrylate monomers at 6164 cm⁻¹ in near-IR region, the sensitizing efficiencies of both dyes were determined. Similar results were obtained (Figure 6b) to the photobleaching experiment, which further confirmed that **4-DAC** exhibited higher sensitizing efficiency than **3-DAC**.

Two-Photon Polymerization. For comparison, three resins (R1-R3) with different components were investigated. The polymerized components of these resins were the same as the OPP resins except for the initiating components. R1 contained 0.4 wt % 3-DAC, 1 wt % HABI, and 1 wt % MMT. R2 and R3 contained 0.4 wt % 3-DAC and 4-DAC, respectively. Their efficiency at initiating the polymerization of the mixed acrylate monomers SR339, SR444, and CN124A80 (m_{SR339}:m_{SR444}: $m_{CN124A80} = 1:3:5$) were characterized by TPP. The threshold energies $(E_{\rm th})$ of the resins were determined using a line scan method.⁴² Here, $E_{\rm th}$ was defined by the lowest laser power at the focus point that ensures the production of a solid line at a line scan speed of $10 \,\mu$ m/s. 2D nanopatterns were fabricated in the resins by changing the incident energy. The lowest $E_{\rm th}$ of 22 μ W was obtained by R1 (Figure 7d). As far as we know, this is the lowest threshold energy ever reported for TPP.

It is found that **3-DAC** and **4-DAC** can also be directly used as single component initiators for TPP. The E_{th} of R2 and R3 were 99 and 198 μ W, respectively, larger than the E_{th} of R1, but also comparatively small among reported results. Compared

TABLE 3: Dipole Moments (μ), Slope (m) and Correlation Factor (r) of Compounds in Mixed Solvents^{*a*}

molecule	a (Å)	$m_1 ({\rm cm}^{-1})$	$m_2 ({\rm cm}^{-1})$	$\mu_{\rm g}$ (D)	$\mu_{\rm e}$ (D)	$\Delta \mu$ (D)	r
3-DAC	6.4^{b}	1852.9	3601.5	3.3	10.3	7.0	0.989, 0.996
	6.3 ^c	1852.9	3601.5	3.2	10.0	6.8	
	5.9^{d}	1852.9	3601.5	2.9	8.9	6.0	
4-DAC	6.0^{b}	2033.1	5078.8	5.0	11.6	6.6	0.958, 0.996
	6.4 ^c	2033.1	5078.8	5.5	12.8	7.3	
	5.7^{d}	2033.1	5078.8	4.6	10.7	6.1	

^{*a*} *a* is the Onsager radius of solute; $\Delta \mu$ is the change of dipole moment between ground state (μ_g) and the first excited state (μ_e). ^{*b*} B3LYP/6-31G(d). ^{*c*} B3LYP/6-31+G(d). ^{*d*} HF/6-31G(d).



Figure 4. Two-photon excitation spectra of 3-DAC and 4-DAC in chloroform.



Figure 5. Cyclic voltammograms of **3-DAC** and **4-DAC** using a Pt electrode at a scan speed 100 mV/s. The solutions contained 0.5 mmol/L of the compounds in acetonitrile with 0.1 M TBAPF₆ as the supporting electrolyte.

to R1, R2 has obvious the advantages of a limited amount of residue of small molecules left after polymerization. Normally, 1-2 wt % of the initiators are used in reported TPP materials. Here, only 0.4 wt % of initiator is used in R2, which evidently decreases the residue of small molecules. In addition, the line fabricated by TPP line in R2 is thinner than that of R1 at the same laser energy (shown in Figure 7, panels c and a), so a much higher resolution is obtained.

It was also found that the incident energy has a significant effect on the width of the fabricated lines (Figure 7, panels a and b). The width of the fabricated lines reduced dramatically as the average laser power decreased. A 3D giraffe with fine

TABLE 4: Electrochemical Data, Absorption Maxima, and $\Delta G_{\rm et}$ of the Dyes to the Initiator

compound	3-DAC	4-DAC	Omnicat 820(E _{red})
$\lambda_{\max} (nm)^a$	495	457	
$E_{\rm ox}$ (V)	0.88	0.96	-0.50
$\Delta G_{\rm et}$ (kcal/mol)	-26.7	-29.7	

^a Data in acetonitrile.



Figure 6. (a) Photobleaching of dyes with Omnicat 820. [Dye] = 2×10^{-5} mol/L, [Omnicat 820] = 8×10^{-5} mol/L in chloroform protected with N₂; (b) Double-bond conversion rate vs irradiation time of dyes with Omnicat 820.

structure was successfully fabricated in R2 at an energy of 163 μ W and a scan speed of 110 μ m/s (Figure 7e). These results indicate great potential for the application of **3-DAC**, **4-DAC**, and their corresponding resins in TPP.

Calculated Molecular Geometries and Electronic Spectra. To learn more about the structure—property relationship of these dyes, the ground state geometry and excited-state properties of 5176 J. Phys. Chem. A, Vol. 114, No. 15, 2010



Figure 7. 2D nanopattern fabricated in (a) R2 and (b) R3 by changing the incident energy with a fixed line scan speed of 10 μ m/s; in R1 by changing (c) the incident energy and (d) the incident energy and adjusting the focal point. (e) 3D giraffe structure fabricated in R2 at a power of 163 μ W and a scan speed of 110 μ m/s. (a-d) Labels show the incident energy (mW) and line width (nm) respectively.

3-DAC and **4-DAC** were determined by theoretical calculations, and the numbering systems for these two compounds are indicated in Figure 8. The optimized dihedral angles of various moieties are listed in Table 5, from which one can reveal that the optimized geometries by Hatree-Fock (HF) and DFT (B3LYP functional) are slightly different. HF method predicts **3-DAC** and **4-DAC** as a less-conjugated structure, in which the largest torsional angle (out of plane) is about 50°. The reason for this is probably due to that HF neglects the electron correlations. Although the geometric parameters of 3-DAC and 4-DAC are not very dependent on the solvents and basis sets employed, the calculated dipole moments are quite sensitive to the basis sets, solvents, and calculation methods (see Table 6). B3LYP-SCRF/6-31G(d) calculation obtained the dipole moment for 3-DAC to be 3.4 D in toluene solution, which is in good agreement with the value (3.3 D) calculated from eq 5. The configuration of **3-DAC** is more planar than **4-DAC**, exhibiting the potential for good polarizability. The dipole moments for 4-DAC calculated by different methods, solvents, and basis sets range from 6.9 to 10.7 D, with a little bigger deviation from the value calculated with eq 5. This gap might be caused by the approximation of eq 5, the accuracy of the data for fitting the line, and accuracy of DFT calculation for the dipole moment. However, the most important is the relative dipole moment, that is, the transition dipole moment from ground to excited states, which can be calculated with TD-DFT method.

The calculated excitation energies (λ_{\max}^a), their corresponding oscillator strengths (*F*), and ground to excited state transition electric dipole moments ($\Delta \mu$) for **3-DAC** and **4-DAC** are listed in Table 6, along with the measured first absorption spectra data for comparison. One can observe from this Table that the transition electric dipole moments for **3-DAC** is bigger than that of 4-DAC, the same trend as calculated from eqs 5 and 6 (see Table 3). For **3-DAC**, the excitation energies, obtained from TD-B3LYP-SCRF/6-31G(d) calculations at B3LYP-SCRF/6-31G(d) geometries, are in good agreement with experimental observations. For 4-DAC, the excitation energies with the same calculation methods are slightly different from the experimental values, which is about 40-60 nm. However, when the geometries obtained with HF-SCRF/6-31G(d) are employed, the calculated excitation energies are quite close to the experimental values. As we know, 3-DAC exhibits a high degree of conjugation, the B3LYP method that fully considers electronic correlation reasonably predicts the real molecular structure of **3-DAC**. However, for the structure of **4-DAC**, the calculated excitation energies are sensitive to the dihedral angle of the coumarin moiety and the central cyclopentanone fragment. The smaller the dihedral angle, the bigger the energy gap between HOMO and LUMO, that is, the bigger the excitation energy. For example, when we rotated the coumarin fragment along the C_8-C_{18} bond for making the dihedral angle $C_1C_8C_{18}C_{19}$ change from 156 to 120° and kept other geometric parameters unchanged, the first excitation energy of 4-DAC calculated in chloroform changes from 507 to 470 nm, which is very close to the experimental value (471 nm) in chloroform solution. The rotation barrier along the C_8-C_{18} bond is very low (about 1 kcal/mol), but the rotation along the corresponding bond of **3-DAC** is not so easy because it will cost more than 6 kcal/ mol energy barrier. Therefore, it is reasonable to presume that the structure of 4-DAC should be even less conjugated than what the DFT calculation obtained, and the structure of 3-DAC could be more coplanar; this is waiting for the further confirmation from the experiments. This can also be observed that the B3LYP-SCRF/6-31G(d) calculation in chloroform solvent pre-



	4-DAC
Figure 8.	The numbering systems of 3-DAC and 4-DAC for all the calculations

IABLE 5: Calculated Dinedral Angles (°) of the Ground States of 3-DAC and 4-DAC at various Calculation Nieth

	HF-SCRF/6-31G(d)	B3L	YP-SCRF/6-31G	(d)	B3LY	G(d)	
	С	Т	Α	С	Т	Α	С
			3-DAC				
$O_7C_5C_4C_6$	6.1	2.8	2.2	2.3	2.8	2.7	2.8
$C_5C_4C_6C_{10}$	-179.3	-178.7	-178.9	-178.8	-178.7	-178.3	-178.5
$C_4C_6C_{10}C_{28}$	-167.3	-175.5	-176.1	-175.8	-175.5	-175.7	-174.8
$O_7 C_5 C_1 C_8$	11.6	7.7	7.6	7.2	7.7	9.4	9.1
$C_5C_1C_8C_9$	176.7	177.2	177.3	177.3	177.2	177.4	176.9
$C_1C_8C_9C_{11}$	-147.3	-154.4	-155.3	-157.2	-154.4	-150.6	-151.4
$C_{27}C_{26}N_{29}C_{31}$	7.0	5.5	4.7	5.3	5.5	4.0	5.1
$C_{25}C_{26}N_{29}C_{30}$	-173.3	-174.7	-175.5	-174.9	-174.7	-176.2	-175.2
$C_{26}N_{28}C_{30}C_{31}$	-179.7	-180.0	-179.9	-180.1	-180.0	-180.0	-180.2
$C_{17}C_{18}N_{21}C_{22}$	-5.5	-5.5	-4.5	-5.8	-5.5	-4.2	-4.4
$C_{19}C_{18}N_{21}C_{23}$	177.4	174.6	175.5	174.8	174.6	175.7	175.6
$C_{18}N_{21}C_{22}C_{23}$	-179.4	-179.6	-179.8	-179.6	-179.6	-179.9	-179.7
			4-DAC				
$O_7 C_5 C_4 C_6$	-6.7	-3.0	-2.1	-2.7	-2.7	-2.3	-2.5
$C_5C_4C_6C_9$	179.8	178.7	178.1	178.2	178.2	178.0	178.0
$C_4C_6C_9C_{10}$	166.0	174.1	175.1	175.0	175.0	175.1	174.9
$O_7 C_5 C_1 C_8$	-10.9	-9.6	-11.3	-10.4	-10.2	-11.4	-11.0
$C_5C_1C_8C_{18}$	-178.2	-177.8	-177.5	-177.7	-177.7	-177.8	-177.8
$C_1C_8C_{18}C_{19}$	132.7	151.0	146.9	148.2	149.6	145.9	147.5
$C_{11}C_{12}N_{15}C_{17}$	6.0	5.5	4.4	5.0	5.8	3.8	4.8
$C_{13}C_{12}N_{15}C_{16}$	-173.5	-174.5	-175.3	-174.7	-173.8	-175.9	-174.9
$C_{12}N_{15}C_{16}C_{17}$	-179.6	-179.8	-180.0	-180.0	-180.0	-180.1	-180.1
$C_{27}C_{26}N_{28}C_{30}$	5.0	4.7	4.0	4.1	4.4	3.3	4.0
$C_{25}C_{26}N_{28}C_{31}$	-174.6	-174.9	-175.6	-175.5	-175.3	-176.4	-175.6
$C_{26}N_{28}C_{30}C_{31}$	-179.4	-179.3	-179.7	-179.5	-179.2	-179.7	

^{*a*} **T**: toluene; **A**: acetonitrile; **C**: chloroform.

dicts that the LUMO orbital of **4-DAC** is lower than that of **3-DAC**, as depicted in Figure 9, indicating that TD-DFT calculation on B3LYP-SCRF/6-31G(d) geometries would underestimate the first excitation energy of **4-DAC**. Furthermore, the calculated oscillator strength of first transition (HOMO \rightarrow

LUMO) of **4-DAC** is significantly smaller than that of **3-DAC**, which is in good agreement with experimental data that the molar absorption coefficient of **4-DAC** is smaller than that of **3-DAC** (see Figure 2). It should be noted that **4-DAC** has another absorption peak around 330 nm in Figure 2, which



Figure 9. Electron density plots of HOMO-1, HOMO, LUMO, and LUMO+1 of 3-DAC and 4-DAC.

corresponds to the excitation between HOMO and LUMO+1 (the fourth excited state). TD-DFT-SCRF calculation in chloroform has also confirmed this peak, and the ratio of the oscillator strength for this excitation over the first excitation is only 0.86, roughly similar to the ratio of the peak heights in Figure 2. The oscillator strength is proportional to the transition electric dipole moment, as indicated in Table 7, which is in good agreement with the traditional point-view.

The dihedral angle between cyclopentanone and coumarin moieties is larger in **4-DAC** than in **3-DAC** (Table 5), and thus the electron densities of the frontier orbitals for **4-DAC** are much more localized than those of **3-DAC** (see Figure 9). The

TABLE 6: The dipole moments (D) calculated with different basis sets

	3-1	DAC	4-DAC			
	6-31G(d)	6-31+G(d)	6-31G(d)	6-31+G(d)		
gas tolunene chloroform acetonitrille	3.8 3.4 6.1 7.2	4.7 6.4 7.8 9.0	6.9 8.4 9.6 10.7	7.6 9.4 10.7 12.1		

transition from its ground state to excited state might result in a large conformational change, which can explain the larger Stoke's shift of **4-DAC** compared with that of **3-DAC** in Figure 2. At present, it is still difficult to calculate the geometric parameters of the excited state for such big system, and thus we cannot calculate the fluorescence spectra for comparison in this paper.

TPA in **3-DAC** and **4-DAC** might correspond to the second excited state (S2), which is mainly the transition from HOMO–1 to LUMO in our calculation. It is clear that TPA cross-section should be related to the transition dipole moments ($\Delta\mu$) and oscillator strength of second excited state. The data in Table 7 indicate that the value for **3-DAC** are obviously larger than that of **4-DAC**, as we expected that the larger change in conformation for **4-DAC** could be happened compared with that of **3-DAC**.

Conclusion

Photophysical and photochemical studies show that both **3-DAC** and **4-DAC** possess strong polarizability. **3-DAC** shows increased conjugation and larger TPA cross sections, whereas **4-DAC** exhibits higher sensitizing efficiencies in OPP. Electrochemical experiments show that **4-DAC** exhibits a lower electron transfer free energy with Omnicat 820, explaining its higher sensitizing efficiency than 3-DAC. Theoretical calculations show great differences in the configuration, electron density, and electron distribution between **3-DAC** and **4-DAC**. **3-DAC** has a near-planar conformation while the conformation of **4-DAC** is twisted. The difference of conformations between **3-DAC** and **4-DAC** will result in different transition electric dipole moments and oscillator strength, which accounts for the smaller one-photon and two-photon absorption coefficients of **4-DAC** compared with those of **3-DAC**.

TABLE 7: Calculated Absorption Maxima, Transition Electric Dipole Moments, and Oscillator Strengths (*F*) of 3-DAC and 4-DAC at the TD-B3LYP-SCRF/6-31G(d) Level of Theory in Various Solvents, along with the Experimental Absorption Maxima Values^{*a*}

solvent	toluene			acetonitrile			chloroform		
				3-DAC ^l	>				
$\Delta \mu$ (D)	13.3(1)		5.9(2)	13.6(1)		4.8(2)	13.3(1)		5.4(2)
$\lambda_{\rm max}^{\rm a}({\rm calc})$ (nm)	499		426	509		436	502		431
F	1.675		0.390	1.715		0.242	1.653		0.316
$\lambda_{\rm max}^{\rm a}({\rm exp})$ (nm)	484			495			500		
4-DAC^b									
$\Delta \mu$ (D)	9.8(1)	$2.7^{(2)}$	6.5(4)	$10.1^{(1)}$	$2.6^{(2)}$	7.7(4)	$10.0^{(1)}$	2.6(2)	7.7(4)
$\lambda_{\rm max}^{\rm a}({\rm calc})$ (nm)	497	487	350	518	500	359	507	492	354
F	0.902	0.071	0.561	0.919	0.066	0.768	0.919	0.065	0.787
$\lambda_{\max}^{a}(\exp)$ (nm)	449			458			471		
4 -DAC c									
$\Delta \mu$ (D)	8.9(1)	$2.2^{(2)}$	6.3(4)	9.0 ⁽¹⁾	$2.3^{(2)}$	$5.9^{(4)}$	9.0(1)	$2.2^{(2)}$	5.7(4)
$\lambda_{\rm max}^{\rm a}({\rm calc})$ (nm)	451	445	333	471	460	345	463	453	339
F	0.822	0.053	0.556	0.816	0.053	0.474	0.827	0.020	0.510

^{*a*}(1), (2) and (4) refer to the first, second and fourth excited states, respectively. ^{*b*} TD-B3LYP-SCRF/6-31G(d) calculation based on B3LYP-SCRF/6-31G(d). ^{*c*} TD-B3LYP-SCRF/6-31G(d) calculation based on HF-SCRF/6-31G(d).

Coumarin/Benzylidene Cyclopentanone Dyes

Furthermore, the application of these two dyes in TPP was studied. **3-DAC** and **4-DAC** can be used directly as photoinitiators in TPP, and the threshold energies of the corresponding resins are as low as the best results reported. High-resolution 2D and 3D nanopatterns containing low amounts of small molecule residue were successfully fabricated by TPP. These dyes should be useful for devices or materials fabricated by TPP that are currently limited by the presence of small molecule impurities.

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