

## Multi-Maleimides Bearing Electron-Donating Chromophores: Reversible Fluorescence and Aggregation Behavior

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Maleimides have been widely used as important monomers, cross-linking and labeling groups in polymer chemistry, biological and pharmacological applications because of their high reactivity toward amine, alcohol, or thiol groups via Michael addition, and cyclopentadiene or furan via [4 + 2] Diels–Alder addition.<sup>1</sup> One interesting feature of this Diels–Alder reaction is its thermal reversibility.<sup>2</sup> A retro-Diels–Alder addition readily occurs at an elevated temperature. Several strategies have been developed for the application of the Diels–Alder addition to envisage various macromolecular architectures: (1) Diels–Alder polycondensation between bis-maleimides and difurans can obtain linear reversible copolymers,<sup>3a</sup> even optically active polymers;<sup>3b</sup> (2) thermoreversible highly cross-linked networks including hydrogels and interpenetrating polymer networks could be prepared from the Diels–Alder reaction between the polymers bearing maleimide or furan moieties;<sup>4</sup> (3) Diels–Alder reaction has also been used for polymer chain extension by the reaction between two moieties with maleimide or diene end groups.<sup>5</sup> More recently, McElhanon et al. reported thermally cleavable/reassembling dendrons and dendrimers based on furan–maleimide Diels–Alder reactions.<sup>6</sup> However, little attention was paid to the photophysical and photochemical properties, as well as aggregation behavior during Diels–Alder addition.

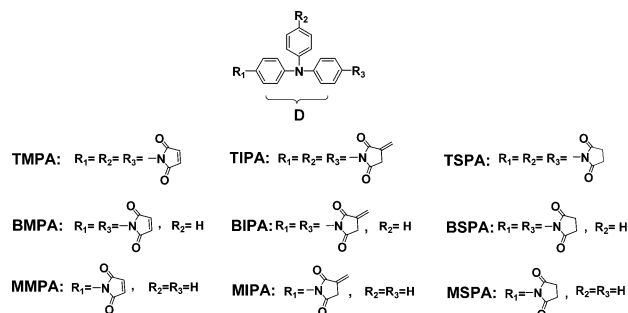
In this study, we synthesize a series of maleimides bearing triphenylamine chromophore, their model compounds and corresponding itaconimides (Chart 1). These mono-, bis-, and tris-maleimides and itaconimides are symbolized as  $A_{(=)}-D$ ,  $[A_{(=)}]_2-D$  and  $[A_{(=)}]_3-D$ , respectively, where D denotes the electron-donating chromophore,  $A_{(=)}$  denotes the electron-accepting moieties containing C=C bonds.

The synthetic routes and characterization of these compounds are provided in Supporting Information. TMPA, TSPA, TIPA, MIPA, MSPA are new compounds. The single-crystal X-ray analyses indicate that TMPA and TSPA have a  $C_3$  centro-symmetrical propeller-like geometry arrangement with the center N–C bonds lying in one plane. These maleimides tend toward a more planar structure than their model compounds due to the enhanced electron delocalization interaction.<sup>7</sup>

The absorption at 310.1 nm ( $\pi-\pi^*$  transition) of these maleimides and their model compounds in 1,2-dichloroethane (DCE) was found to decrease gradually in the order of TSPA > TMPA > TIPA, BSPA > BMPA > BIPA, MSPA > MMPA > MIPA (Figure S-8). A weak broad absorption band at 439.1 nm increased gradually in an opposite order. The concentration independence of the broad absorption of TMPA in DCE and its disappearance in methanol (Supporting Information Figures S-9, S-14) reveal that the broad absorption results from an intramolecular charge transfer (ICT).

Model compounds MSPA, BSPA, and TSPA display a strong fluorescence at 375 nm in DCE. Their fluorescence quantum yields and lifetimes determined from steady-state and time-resolved

Chart 1

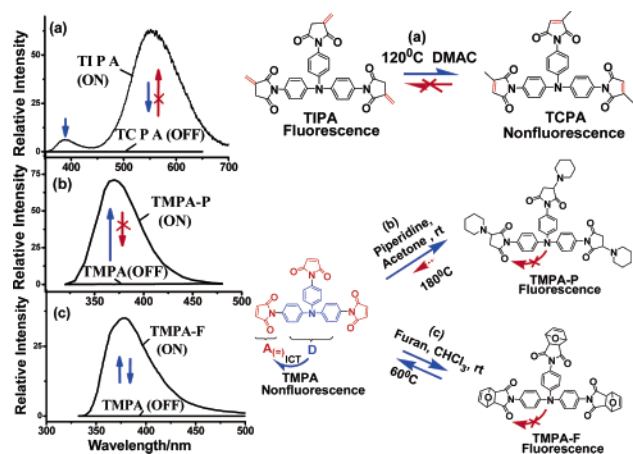


fluorescence spectroscopy are 0.057 and 0.85 ns for TSPA, 0.069 and 1.12 ns for BSPA, 0.051 and 0.82 ns for MSPA, respectively. However, almost no fluorescence was observed for MMPA, BMPA, and TMPA. This suggests that the C=C bonds of maleimide group have a significant fluorescence quenching effect.

Compared with these maleimides, MIPA, BIPA, and TIPA display a moderate fluorescence quenching at 375 nm. A new broad structureless emission peak appears at 551 nm with short lifetime: 0.26 ns for MIPA, 0.36 ns for BIPA, 0.39 ns for TIPA. The broad emission increases gradually from MIPA, BIPA, to TIPA as the emission at 375 nm decreases (Figure S-11). According to their absorption and excitation spectra (Figure S-13), the broad emission is attributed to an ICT interaction between excited donor and  $A_{(=)}$ . Time-resolved fluorescence spectrum of TIPA indicates that the emission at 551 nm initially increases as the emission decays at 375 nm (Figure S-17). This result confirms the ICT mechanism between  $A_{(=)}$  and D.

It should be noted that the ICT interaction is distinct from the intermolecular interaction. There is only a slight intermolecular fluorescence quenching of triphenylamine by maleimide even in 1:30 molar ratio, where no new broad emission or absorption band was observed (Figure S-15).

It is interesting to see that, after the *N,N*-dimethyl acetamide (DMAC) solution ( $5 \times 10^{-5}$  M) of TIPA was heated at 120 °C for 2 h, its fluorescence disappeared (Figure 1a). <sup>1</sup>H NMR spectra indicate that TIPA was isomerized into the corresponding tris-citraconimide TCPA. The same phenomenon was observed for MIPA and BIPA. The citraconimide group is an  $\alpha$ -methyl maleimide analogue. Electrochemical data obtained from cyclic voltammetry indicate that the citraconimide ( $EA = 0.571$  eV) and maleimide (0.565 eV) groups possess a stronger electron-accepting ability than itaconimide acceptor (1.16 eV) according to their electron affinity (EA).<sup>8a</sup> The changes in the free energy ( $\Delta G$ ) of charge transfer determined from the Rehm–Weller equation<sup>8b</sup> indicate that the extent of ICT increases in the order of BIPA ( $\Delta G = -1.72$  eV), BCPA ( $\Delta G = -1.86$  eV), BMPA ( $\Delta G = -1.88$  eV); and TIPA ( $\Delta G = -1.82$  eV), TCPA ( $\Delta G = -1.95$  eV), TMPA ( $\Delta G = -1.98$  eV). Therefore, the isomerization process



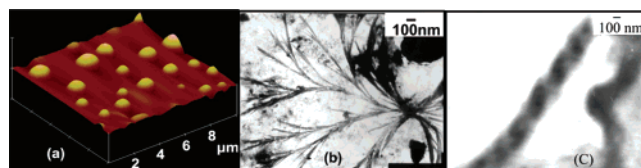
**Figure 1.** Irreversible fluorescence spectra and schematic illustration for the isomerization of TIPA in DMAC (a), Michael addition of TMPA with piperidine (b), and reversible fluorescence spectra for Diels–Alder addition of TMPA with furan in chloroform (c).  $\lambda_{\text{ex}} = 310.0$  nm.

causes a stronger ICT interaction between  $A_{(=)}$  and D, which leads to a significant fluorescence quenching. During the isomerization, the fluorescence is switched from “ON” to “OFF” (Figure 1a). However, this fluorescence behavior is irreversible.

Michael and Diels–Alder additions are two typical reactions related to the electron-accepting C=C bonds of maleimides.<sup>1</sup> Michael addition of TMPA with piperidine was carried out in acetone at room temperature. As the Michael addition proceeds, the electron-accepting C=C bonds are consumed. The deactivated ICT pathway is closed, which leads to the fluorescence switched from “OFF” to “ON” (Figure 1b). The fluorescence switch is also irreversible. A retro-Michael addition is difficult, which can only occur at 180 °C.<sup>9</sup>

Diels–Alder adduct of TMPA with furan (*exo,exo,exo*-TMPA-F)<sup>10</sup> also displays a strong fluorescence at 375 nm. Although a new C=C bond was formed in the adduct TMPA-F, it does not show any fluorescence quenching. This result supports that the fluorescence quenching is only due to the electron-accepting C=C bond, which can interact with donor in excited state. At 60 °C, a retro-Diels–Alder addition readily occurs in TMPA-F to give out furan, where the electron-accepting C=C bond is formed again. Therefore, for TMPA, the deactivated ICT pathway is open between  $A_{(=)}$  and D, and its fluorescence is switched in an “OFF” state. For TMPA-F, the ICT pathway is closed, and its fluorescence is switched in an “ON” state. The two states are reversible due to a reversible Diels–Alder addition leading to a reversible opening and closing of the ICT pathway. To the best of our knowledge, this is the first report on the reversible fluorescence behavior based on the Diels–Alder reaction.

The Diels–Alder adduct of TMPA with furfural alcohol (*exo,exo,exo*-TMPA-FA)<sup>10</sup> was found to self-organize into spherical aggregates (1.0 mg/mL) and dendritic morphology (10 mg/mL) in deionized water (Figures 2a,b, S-20, and S-21). In ethanol, interestingly, helical morphology was observed (Figures 2c and S-21). The helical formation may be due to the inducing effect of the propeller-like structure of the TSPA core. The detailed study on the aggregation behavior is underway. These aggregates display a strong fluorescence at 378 nm. More interestingly, these aggregates disappeared at the elevated temperature of 75–80 °C. A red precipitate appeared, and no fluorescence was observed. Spectral



**Figure 2.** AFM image (1.0 mg/mL, water (a)) and TEM images (10 mg/mL, water (b); 1.0 mg/mL, ethanol (c)) of the *exo,exo,exo*-TMPA-FA aggregates.

data confirm that the red precipitate is TMPA, suggesting that a retro-Diels–Alder reaction occurred. After the above solution was stirred at room temperature for 6 h, the red precipitate disappeared. These aggregates were observed again (Figure S-20), and the fluorescence was restored. The same aggregation behavior was also observed for a mixed *exo,exo,exo*-*endo,endo,endo*-TMPA-FA (1.0/0.59). To the best of our knowledge, this is the first report on the reversible aggregation accompanied with reversible fluorescence behavior based on the Diels–Alder addition of maleimides.

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**Supporting Information Available:** Synthetic routes, characterization, fluorescence and UV–vis spectra, electrochemical data, cyclic voltammograms of MMPA, MSPA, MIPA, BIPA, BSPA, TMPA, TIPA, TSPA and their energy diagrams of photoinduced charge transfer, 2D <sup>1</sup>H–<sup>13</sup>C HSQC NMR spectra of *exo,exo,exo*-TMPA-F and *exo,exo,exo*-TMPA-FA; MALDI-TOF mass spectra of TMPA-F, TMPA-FA, TMPA-P, fluorescence decay curves of MSPA, BSPA, and TSPA, time-resolved fluorescence spectrum of TIPA, and crystallographic data (CIF) of BIPA, BSPA, TMPA and TSPA. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (7) The single-crystal X-ray analyses indicate that TMPA and BIPA display a smaller torsion angle (53.7° and 62.1°) between its phenyl ring and adjacent maleimide ring, and higher crystal density (1.450 and 1.376 Mg/m<sup>3</sup>) than corresponding saturated compounds TSPA (59.2°, 1.432 Mg/m<sup>3</sup>) and BSPA (67.3°, 1.341 Mg/m<sup>3</sup>), respectively.
- (8) (a) Electron affinity was calculated from reduction potential  $E_{\text{red}}(A^-/A)$  of the acceptor using the relationship of Chen (Chen, E. C. M.; Wentworth, W. E. *J. Chem. Phys.* **1975**, *63*, 3183). (b)  $\Delta G = E_{\text{ox}}(D/D^+) - E_{\text{red}}(A^-/A) - E_{00}(D^*) - C$ , where  $E_{\text{ox}}$  is the oxidation potential of the donor,  $E_{00}(D^*)$  is the excitation energy, and C is the electrostatic interaction term.
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- (10) TMPA-F and TMPA-FA obtained initially are a mixed *exo,exo,exo*-*endo,endo,endo*-isomers. The pure *exo,exo,exo*-isomer can be obtained by heating the mixed isomers in chloroform with an addition of furan or furfural alcohol at 40 °C for 2 days, where the *endo,endo,endo*-isomer was converted completely into the *exo,exo,exo*-isomer. The *exo,exo,exo*-isomer is relative stable, which does not reconvert into *endo,endo,endo*-isomer before retro-Diels–Alder occurring.

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