Excited State Dynamics of 2-MPT-Derived Fluorescent Molecular Switches

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Abstract—Excited state dynamics from molecular fluorescent switches of the donor- or acceptor-derived 5-Methoxy-2-(2-pyridyl)thiazole (2-MPT) fluorescent molecules has been studied by ultrafast spectroscopy. The twisted intramolecular charge transfer (TICT) excited state is found to be created within 1 ps. Then the relaxation of TICT excited state causes further twist of the molecular conformation (especially the moiety 2-MPT) and reduces the transition moment. It takes about 600-700 ps to reach a state with ten nanoseconds of lifetime. This final state is nearly a dark state, which is attributed as the main reason for the drastic decrease of the fluorescence quantum field with respect to the moiety 2-MPT. For MPTEA with a strong electron donor in high polarity solvents, TICT's excited state partially transfers to a planar intramolecular charge transfer (PICT) excited state within 10 ps due to the strong dipole-dipole interaction with solvent molecules. PICT's excited state gives a relatively strong emission with a large red shift. The results demonstrate that the excited state dynamics of these molecular fluorescent switches provides deep insight to their photophysical processes, which is important for exploring novel molecular switches as potential candidates for optical biolabels, sensors and logic gates applications.

Index Terms—Excited state dynamics, femtosecond laser, intramolecular charge transfer, molecular switch.

I. INTRODUCTION

THE novel molecular switches have been paid much attention since they can be widely used as optical biolabels, sensors, and logic gates [1]–[11]. Especially, for the molecular fluorescence switch as an optical probe, the changes in either fluorescence intensity or emission position provide zero-background output signal in sensing applications [12], [13]. New molecular fluorescence switches are commonly achieved by deriving the fluorophore with special binding sites, which can bind to specific targets. As a consequence, the binding site will cause the interaction with the fluorophore both in ground and excited states. For example, the electron-rich metal binding sites may donate electrons to the originally fluorophore- centered frontier orbits at the excited states. The charge transfer processes between the fluorophore and the reception site produce new fluorescence switching features, and this behavior is also strongly influenced by the surround environment [14], [15]. Therefore, understanding the derivation-fluorescence correlation is very important for applications using a fluorophore in optical sensing. On the other hand, the relation between molecular conformation change in excited state and its photophysical property is a long standing topic. For example, the characteristics of intramolecular charge transfer (ICT) has been extensively studied in the past 30 years [16]–[24], and twisted intramolecular charge transfer (TICT) model [25]–[27], planar intramolecular charge transfer (PICT) model [28], [29], and models such as $\Delta E(S1, S2)$ playing a crucial role in determining the occurrence of ICT state [30] have been suggested.

5-Methoxy-2-(2-pyridyl)thiazole (2-MPT), a newly developed blue-emissive fluorophore, exhibits high quantum yield in both water and organic solvents [31]. Its derivatives with fluorescence switch behavior can act as various binary logic gates and have an application potential in molecular sensors [32]–[34]. Further application requires detailed understanding on the perturbation of original MPT-centered charge transfer by the reception site. Recently, Sun et al [35] reported the steady-state photophysical properties of donor- or acceptor-derived 2-MPT fluorescent switches, in which the fluorophore and the aromatic substituent are covalently linked to a triple bond [35]. The substitution groups are systematically varied from the strong electron donors to weak donors. Both the steady-state spectral and theoretical investigations have revealed the roles of the substituents in the electronic transitions in 2-MPT derivatives. The conformation relaxation of excited state to either a twisted or a coplanar structure depends on the substituents and also interaction with the solvent molecule, so the final emission state can be either TICT or PICT state. However, the excited state dynamics and detail relaxation path are still unclear. Furthermore, 2-MPT-derived molecular fluorescent switch also is a very good molecular system to understand the photophysical property of ICT, TICT and PICT states. Femtosecond laser technique as an important optical tool has been widely used in studying various nonlinear optical phenomenon [36]–[38] and also is an ideal tool for investigating the above photophysical processes.

In order to further give a full picture of the excited state processes for 2-MPT-derived molecular fluorescent switches, we studied the excited state dynamics for 2-MPT derived fluorescent molecules with weak and strong electronic donor both in toluene and acetonitrile based on the femtosecond
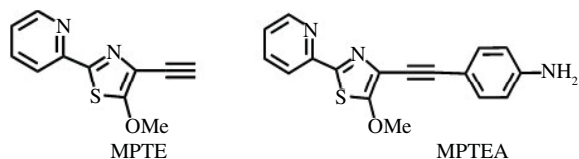
Fig. 1.   Structures of MPTE and MPTEA.

fluorescence up-conversion and transient absorption techniques.

II. Experiments

The procedure for the preparation of the MPTE and MPTEA compounds was as described in Ref. [35] structures shown in Fig. 1. The solvents toluene and acetonitrile, are of spectrophotometric grade (Aldrich). Samples with a concentration of 10^{-4} M were used for the measurements.

Femtosecond fluorescence upconversion kinetics were measured by means of the set-up described previously [39]. The pump (at 350 nm) is generated by the laser system (Spectra-Physics, 800 nm pulse, 150 fs pulse duration, and OPA-800 C). The system response time as measured from the cross-correlation signal of the excitation and gating pulses at 350 nm and 800 nm, was estimated to be approximately 450 fs (FWHM). In the femtosecond transient absorption experiments [40], the same laser system was used, while the probe is a white light continuum pulse generated by focusing the 800 nm beam into a sapphire plate. Time resolved transient absorption spectra were detected with a highly sensitive spectrometer (Avantes AvaSpec-2048×14). The group velocity dispersion of the whole experimental system was compensated by a chirp program. To remove contributions from rotational reorientation motions of the solute molecules, measurements were performed under magic angle conditions (with the laser-excitation polarization at an angle of 54.7° relative to the vertically polarized gating beam or white light continuum).

Steady state absorption spectra were measured by a Shimadzu UV-1700 spectrophotometer, and emission spectra were recorded with a Shimadzu RF-5301PC spectrometer. All experiments were performed at room temperature.

III. Results and Discussions

A. Steady-State Absorption

Figure 2 shows the steady-state absorption and fluorescence spectra of MPTE and MPTEA in toluene and acetonitrile solvents. For MPTE, the absorption peaks locate at 337 and 334 nm corresponding to the $S_0 \rightarrow S_1$ electronic transition in toluene and acetonitrile, respectively. The emission peaks emerge at 405 and 410 nm in toluene and acetonitrile, respectively, and the fluorescence band only show slightly red-shifted with the increase in solvent polarity. As for MPTEA, absorption peaks are around 356 nm for both in toluene and acetonitrile. However, comparing with MPTE, the fluorescence emission strongly depends on the solvent polarity. The emission peak is red-shifted from 444 nm in toluene to 520 nm in acetonitrile with significant broadening of the emission band, which indicates that MPTEA with a strong electronic
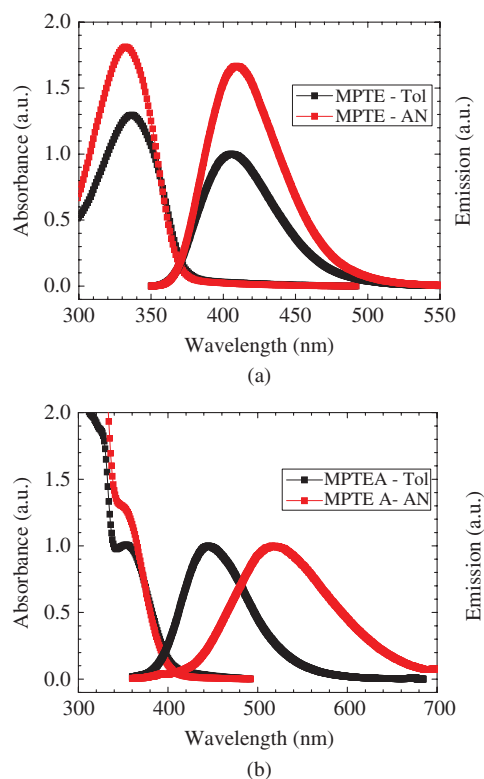

Fig. 2.   Steady-state spectra. (a) MPTE in toluene and acetonitrile. (b) MPTEA in toluene and acetonitrile

donating substituent tends to produce a larger excited state dipole moment and results in the stronger interaction with the solvent molecules, thus causes the significant red-shifted of emission band.

Theoretical calculations indicate that intramolecular charge transfer (ICT) state exists for both MPTE and MPTEA with twisted excited state conformations [35], of which the fluorescent switching functions applied in digital logic circuits also have been described in elsewhere publications [32]–[34]. The electronic transition from the local excited (LE) state to the twisted ICT (TICT) excited state occurs very fast, so the emission mainly comes from the TICT state. But for MPTEA, its aromatic ring with amino group can rotate around the triple bond axis after excitation. So if there is enough energy to activate the rotation freedom, a planar configuration that the substitute and MPT moiety keep good planarity in the excited state called the planar ICT (PICT) state may be produced, which leads to the excited state configurationally change from the TICT to the PICT state and results in the fluorescence lifetime of PICT state longer than that of TICT excited state. For MPTEA in low polarity solvents such as toluene, the emission originates from the TICT state, while in high polarity solvents such as acetonitrile there is an excited state configurational change from the TICT to PICT excited state resulting in the broadening and red-shifted of the emission band, thus the fluorescence band for MPTEA in acetonitrile is the superposition of the TICT and PICT fluorescence.

In order to further verify the above results from the experimental aspects and also give a full picture of the processes,
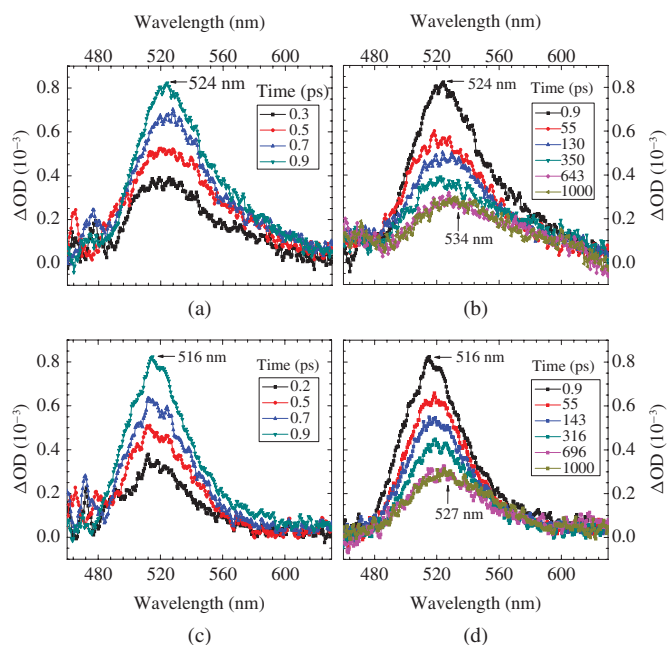
Fig. 3. Time-resolved transient absorption spectra for MPTE in toluene and acetonitrile, respectively. (a) and (b) MPTE in toluene. (c) and (d) MPTE in acetonitrile.

we studied the relaxation processes of excited states for MPTE and MPTEA both in toluene and acetonitrile based on the femtosecond fluorescence up-conversion and transient absorption techniques.

B. Time-Resolved Transient Absorption

Fig. 3(a) shows the transient absorption spectra for MPTE in toluene during the first picosecond. One can clearly see that the excited state absorption (at 524 nm) is not instantaneously formed after the excitation, which the formation time is about 300 fs. Then the absorption spectrum decays gradually accompanied by a peak shift during the relaxation process (Fig. 3(b)). The absorption peak shifts from 524 nm at 0.9 ps to 532 nm at 650 ps. After then, the spectrum keeps the shape and no longer decay. The normalized transient absorption dynamics at 524 nm exhibits a constant component in nanosecond time scale with amplitude about 25%. The time resolved transient absorption spectra of MPTE in acetonitrile are shown in Fig. 3(c) and Fig. 3(d). It is quite similar to that in toluene. The excited state absorption (at 516 nm) is formed with a time constant about 300 fs. And then, the excited state absorption band shift from 516 to 527 nm during the decay. After 700 ps, the spectrum is nearly no change and decay, which the amplitude of this constant component is about 25%.

For MPTEA in toluene, the excited state absorption (at 540 nm) is formed with a time constant about 250 fs, and spectra show a significant blue shift during the formation, which the peak shifts from 560 nm at 0.1 ps to 540 nm at 0.7 ps (Fig. 4(a)). And then, the absorption spectrum gradually decays also accompanied by a peak shift to 552 nm at 600 ps (Fig. 4(b)). After that, the spectrum show no longer change and decay.
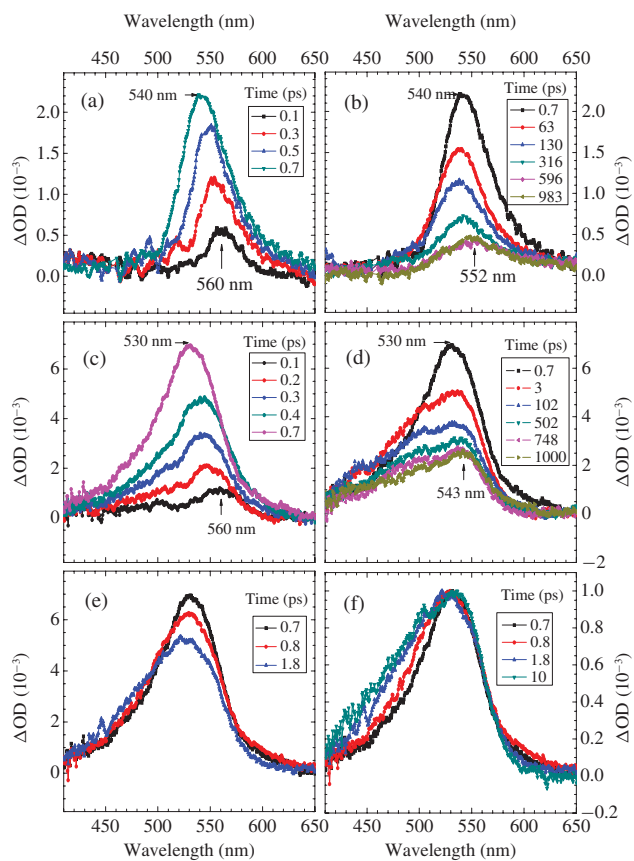

Fig. 4. Time-resolved transient absorption spectra for MPTEA in toluene and acetonitrile, respectively. (a) and (b) MPTEA in toluene. (c)–(f) MPTEA in acetonitrile, where (f) represents the normalized time-resolved transient absorption spectra.

For MPTEA in acetonitrile the formation of the transient absorption signal is similar with that in toluene. There is also a clear blue shift of the absorption spectrum (Fig. 4(c)), and the absorption peak shifts from 560 nm at 0.1 ps to 530 nm at 0.7 ps. However, different from the above three cases, the excited state absorption band at 530 nm shows a fast decay process during the first 10 ps, while a new transient absorption band range from 430 to 510 nm is formed (Fig. 4(e)). The normalized time-resolved absorption spectra show more clearly that the absorption band becomes broader towards the shorter wavelengths during the period of 0.7 ps to 10 ps, and the formation of a new excited state absorption band (Fig. 4(f)). The transient signal is the combination of these two excited state absorption bands. For the band at 530 nm, its relaxation is quiet similar to those in the above three cases. The absorption spectrum gradually decays also accompanied by a peak shift to 540 nm at 700 ps (Fig. 4(d)), and then keep constant. However, the new blue band shows rather slow decay trend that the time constant is about 1.2 ns.

C. Time-Resolved Fluorescence Emission

Finally, the fluorescence upconversion experimental results complementary to those from femtosecond transient absorption experiments have been obtained. Figure 5 shows the normalized fluorescence dynamics for MPTE and MPTEA in toluene and acetonitrile, respectively. All the fluorescence
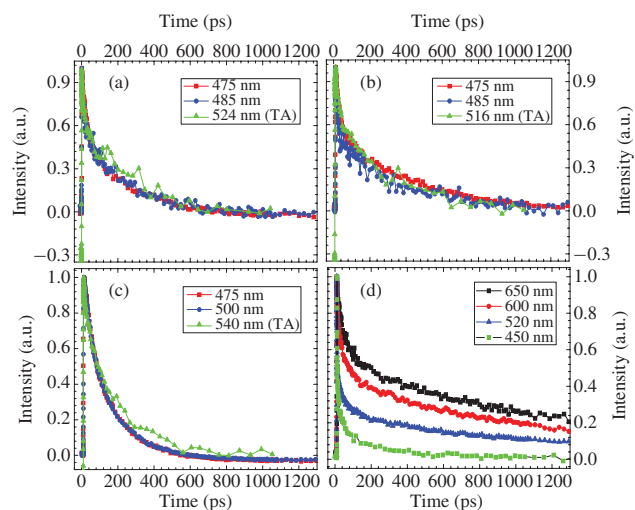
Fig. 5. Fluorescence and transient absorption transients for MPTE and MPTEA in toluene and acetonitrile, respectively. (a) MPTE in toluene. (b) MPTE in acetonitrile. (c) MPTEA in toluene. (d) MPTEA in acetonitrile.
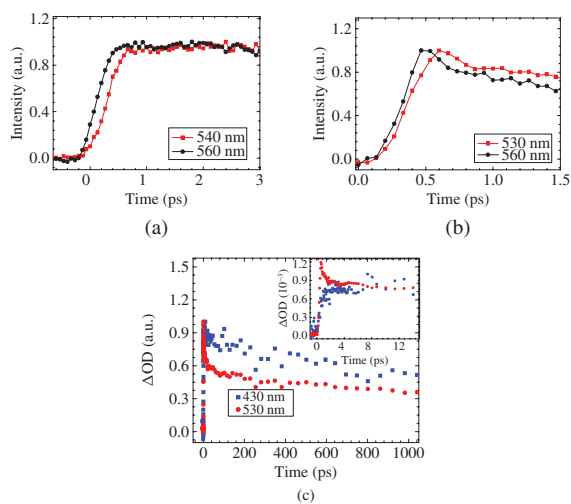

Fig. 6. Normalized transient absorption dynamics in early timescales for MPTEA probed. (a) Toluene. (b) Acetonitrile. The dynamics shows the LE to TICT state transition. (c) Normalized transient absorption dynamics for MPTEA probed at 430 nm and 530 nm in acetonitrile to represent TICT to PICT state transformation.

transients were fitted to multi-exponential functions and were convoluted with the system response function and the best-fit parameters of fluorescence transients are list in Table I.

As for MPTE in toluene and acetonitrile and also for MPTEA in toluene, the fluorescence transients show nearly the same kinetics at different detected wavelength (Fig. 5). The fitting results give two lifetimes, one is around tens picoseconds and another longer one is range from 220 ps to 350 ps (Table 1). We should note that the fluorescence transients perfectly match the excited state absorption kinetics, if we neglect none decay component in the transient absorption experiments (Fig. 5). However, for MPTEA in acetonitrile, the fluorescence dynamics show a very strong wavelength dependent behavior (Fig. 5(d)). As the wavelength increasing, the fluorescence dynamics decays slower gradually. Comparing with the above three cases, the fluorescence transients have a considerable fast decay component that is dominant in blue side (450 nm to 520 nm). The longest lifetime is about 1.2 ns, and the amplitude increases as detected wavelength becomes longer. At the far blue side 450 nm, the 1.2 ns component is absent; the longest lifetime is 220 ps (Table 1).

Actually, time-correlated single photon counting (TCSPC) measurements for MPTE and MPTEA in both solvents show that the emission have a small proportion of long-lived fluorescent component (less than 1%) with tens nanoseconds lifetime (data not shown), which is so weak that is hardly seen in the femtosecond fluorescence up-conversion measurements.

D. Excited State Dynamics of MPTE

For MPTE both in toluene and acetonitrile, the excited state absorption and also fluorescence show a single band behavior with essential same dynamics, which indicates that, the relaxation process comes from one electronic state. However, from the transient absorption experimental results, this state is not instantaneously formed after the excitation, which implies the state transition process. At the early time (the first one picosecond), this transition is corresponding to intramolecular

charge transfer process as expected by theoretical calculation. The transition from the LE state to the TICT state leads to the charge redistribution in the molecules. Then the molecular nuclear conformation will change to stabilize the TICT state, which occurs relatively slower than the electronic transition. From the time-resolved transient absorption spectra, one can see the stabilization of the TICT state is accompanied by the red shift of the excited state absorption band until 600 ps–700 ps, with a evolution lifetime of 200–300 ps. After the relaxation, it is interesting that the excited state population does not completely return back to ground state. The excited state absorption of TICT state shows no decay trend in nanosecond time scale; this implies that the TICT excited state relaxes to a rather stable final state with very long lifetime.

The time-resolved fluorescence experimental results show that this final state gives extremely weak emission, which is a nearly dark state. So, the TICT conformational relaxation process is associated with the decrease of the electronic transition probability and finally forms a twisted dark excited state. Because of the forbidden electronic transition in the dark state, the electrons will stay in the excited state for a very long time, and TCSPC fluorescence dynamics show that the dark state has a lifetime about tens nanoseconds. This kind of dark state is also found in other molecules with twisted excited state, such as auramine [41] and poly(spirofluorene-co-benzothiadiazole) [42]. The relaxation of TICT state causes the further twist of the molecular conformation (especially the moiety 2-MPT) and reduces the transition moment. We believe that the presence of the dark state in 2-MPT derived fluorescent molecules is the main reason for the drastically decrease of the fluorescence quantum field relative to the moiety 2-MPT.

E. Excited State Dynamics of MPTEA

Comparing with MPTE, MPTEA has a much strong electron donor (amino groups), this will results that the intramolecular

Solute	Solvent	Wavelength (nm)	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	τ_4 (ps)
MPTE	Tol	475	26 (45.9%)	276 (54.1%)		
	AN	475	22 (42.7%)	415 (57.3%)		
MPTEA	Tol	475	70 (51.1%)	211 (48.9%)		
	AN	450	1.0 (68.0%)	21 (21.0%)	220 (11.0%)	
		520	1.2 (62.0%)	31 (15.0%)	220 (6.0%)	1200 (17.0%)
		600	2.1 (22.0%)	35 (31.0%)	220 (7.0%)	1200 (39.0%)
		650	4.0 (10.0%)	53 (36.0%)		1200 (54.0%)

Best-fit parameters of femtosecond fluorescence up-conversion dynamics of MPTE and MPTEA in toluene and acetonitrile with function $I \infty \sum_i A_i \exp(-t/\tau_i)$

charge transfer state has a large dipole moment and strong dipole-dipole interaction with solvent molecule. So, the rotation freedoms of aromatic ring with amino group around the triple bond axis can be activated if there is enough energy due to the strong interaction. As a result, a planar configuration that the substitute and MPT moiety keep good planarity in the excited state PICT may be produced.

For MPTEA in toluene, the transient absorption result also shows the transition from the LE state to the TICT state at the first picosecond. The spectra show a significant blue shift during the transition, which may reflect the strong charge transfer character of MPTEA molecule. And then, its behavior is quiet similar to that of MPTE, the relaxation of the TICT state takes about 600 ps, finally reach to dark state with tens nanoseconds lifetime. The time-resolved fluorescence experiments also give consistent results. So, in toluene, there is not enough energy to activate the rotational freedom because toluene molecule is not very polar.

For MPTEA in acetonitrile, at the first picosecond, the transition from the LE state to the TICT state is also observed, while the spectra show a significant blue shift as that in toluene. After that, the excited state dynamics exhibits very different behavior. The fluorescence dynamics is strongly dependent of the detected wavelength. The fitting results indicate that the emission comes from two states, which the lifetimes are 220 ps and 1.2 ns, respectively. At far blue or red side of emission band, the fluorescence only show one long lifetime (Table I). One state with lifetime 220 ps obviously is the TICT state just like the above three cases. As mentioned above, a planar excited state configuration may be produced because of the rotation of the aromatic ring around the triple bond axis after excitation and generates the PICT state. The formation of PICT excited state needs to overcome the energy barrier for the substitute rotating around the triple bond axis. For MPTEA in low polarity solvents such as toluene, the dipole-dipole interaction between the molecule and solvent is not strong enough to overcome the barrier, thus the emission is only from the TICT state. While for MPTEA in high polarity solvents such as acetonitrile, the stronger interaction lows down the energy level of PICT state, and the small barrier makes the PICT state possible. So, another new state with longer lifetime 1.2 ns can be assigned to PICT state with rather strong emission at red side. Therefore, the emission band for MPTEA in acetonitrile is the superposition of the
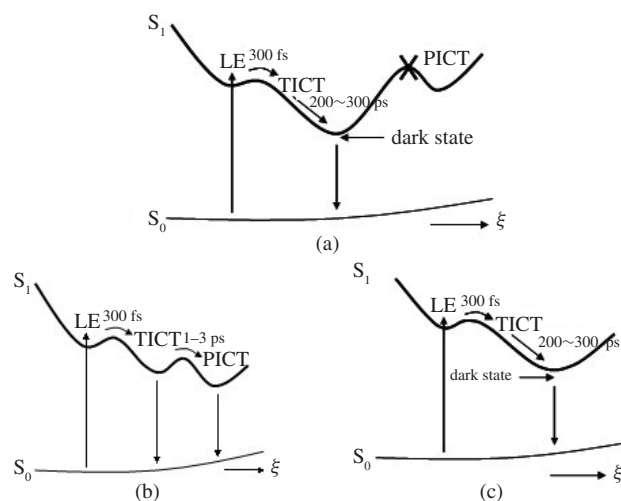

Fig. 7. Schematic representation of excited state dynamic pathways for 5-Methoxy-2-(2-pyridyl)thiazole-derived fluorescent molecules. (a) Less polar solvents. (b) and (c) MPTEA in high polar solvent.

emission from both the TICT and PICT excited states. We can not resolve the clear formation process of TICT from the fluorescence dynamics because of the mixture of two emission bands. However, comparing with the above three cases, the extraordinary fast decay process that the time constants range from 1 ps to 4 ps (Table I), very likely reflects the transition from TICT to PICT.

The transient absorption experiments further confirm this conclusion. The excited state absorption also contains two largely overlapping bands, one at 530 nm corresponds to the TICT state formed with in 1 ps. The time resolved spectra clearly show a state transition process within 10 ps, which the absorption decay of TICT state accompanies with the growing in a new absorption (PICT) around 470 nm (Fig. 4). If we check the transient kinetics at the far blue side like 450 nm, a clear rise process can be resolved and this rise dynamics well agree with 1 ps–4 ps process in the fluorescence transients (Fig. 6(c)). So, after the intramolecular charge transfer [Fig. 6(a) and 6(b)], TICT state partially converts to PICT state within about 10 ps. And then, the two states relax differently reflecting their physical nature. At the blue side, the excited state absorption mainly contributed by PICT state shows relatively slow decay. At 450 nm, the signal
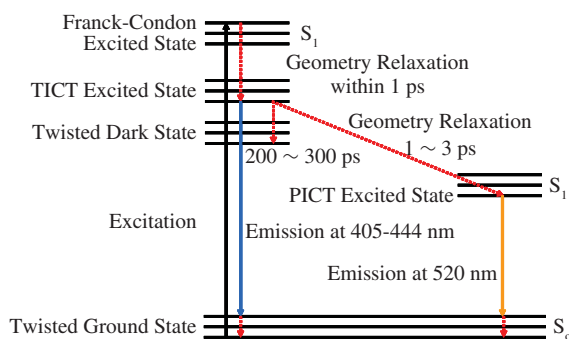
Scheme 1. Scheme for the excitation, geometry relaxation, and emission of the TICT and PICT states in MPTE and MPTEA.

without interference of TICT has a single lifetime 1.2 ns (Fig. 6(c)), which again agrees with the fluorescence result. The excited state absorption at 530 nm (TICT) evolutes just as the above three cases, finally reach the dark state after 600 ps. And the amplitude of the long-lived absorption component for the dynamics at 530 nm is relatively larger due to the contribution from the PICT absorption signals. The full excited state dynamic pathways for MPTE and MPTEA are shown in Fig. 7:(a) represents dynamic pathways for MPTE and MPTEA in less polar solvents; (b) and (c) represent two dynamic processes occurring simultaneously for MPTEA in high polar solvent. In order to explain these processes more clearly, we show the scheme for the excitation, geometry relaxation, and emission of the TICT and PICT states in MPTE and MPTEA in Scheme 1.

IV. CONCLUSION

The excited state dynamics of the donor-or acceptor-derived 2-MPT molecular fluorescent switches has been studied by ultrafast spectroscopy, the full excited state pathways are: (1) LE state transition to TICT state within 1 ps; (2) TICT state partially transformation to PICT state within 10 ps; (3) TICT state stabilization to a twisted dark state during several hundreds picoseconds. Briefly, after excitation, intramolecular charge transfer process creates the TICT excited state within 1 ps. The transition from the LE state to the TICT state leads to the charge redistribution in the molecules. Then the molecular nuclear conformation will change to stabilize the TICT state, it takes about 600 ps–700 ps to reach a state with tens nanoseconds lifetime. The relaxation of TICT state causes the further twist of the molecular conformation (especially the moiety 2-MPT) and reduces the transition moment. The final state is nearly dark state with very small transition moment, which is the main reason for the drastically decrease of the fluorescence quantum field relative to the moiety 2-MPT. For MPTEA with a strong electron donor (amino groups) in high polarity solvents such as acetonitrile, TICT state partially transfer to a planar configuration state PICT within 10 ps due to the strong dipole-dipole interaction with solvent molecule. PICT state gives relatively strong emission with large red shift. The understanding of excited state dynamics is important for exploring novel molecular switches, which can be used in optical biolabels, sensors, and logic gates.

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