Intramolecular charge transfer in donor-bridge-acceptor compounds with paired linearly conjugated or cross-conjugated pathways

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An understanding of intramolecular charge transfer in 2-D linearly conjugated and cross-conjugated compounds is necessary for the rational design of molecular electronics, improved solar energy devices, semi-conducting polymers, and materials with nonlinear optical properties. In this work, the femtosecond transient absorption spectra and kinetics of several donor-bridge-acceptor compounds containing cross-conjugated or linearly conjugated bridging groups were obtained. The veratrole group was used as the donor, and the phthalimide group was used as an acceptor. 2-D conjugation was achieved by involving two bridging groups arranged cyclically between the donor and acceptor. The donor and acceptor were bridged by m-phenylene in the cross-conjugated compounds or 2,5-thiophene in the linearly conjugated compounds. We found slower charge separation times and slower charge recombination times in the compounds containing cyclic cross-conjugated bridging groups than in those containing the cyclic linearly conjugated groups in polar solvent. Charge separation rates that were found to be dependent on solvent were observed in the donor-bridge-acceptor compounds. Copyright © 2014 John Wiley & Sons, Ltd.

Keywords: donor–acceptor macrocycles; charge transfer; cross-conjugation; pump-probe spectroscopy

INTRODUCTION

Upon excitation with light, donor-bridge-acceptor (DBA) molecules can undergo intramolecular charge transfer (ICT) to promote an electron from donor to acceptor by way of a molecular bridge. If the process is photoinduced, light is effectively used to transport charge through a molecule. Such processes are the basis for solar energy devices[1–3] and molecular electronics.[4–7] Rational design of molecular systems for devices and electronics requires fundamental understanding of the ICT process in DBA compounds, and much work has been conducted on the subject, although much still remains to be understood.[8]

In the study of ICT in DBA molecules, the nature of the bridge is of considerable interest, and studies have been performed on bridge length,[9] conformation,[10,11] and type and degree of conjugation.[12] However, few examples of DBA molecules containing multiple conjugation pathways are known.[13–15] In addition to their use as DBA molecules, molecules with 2-D conjugation have been designed for use as fluorescent materials used in sensing,[16,17] for their nonlinear optical properties,[18–20] and for their ability to self-assemble into monolayers.[21–23] The effect of 2-D conjugation (as in conjugated macrocycles) on the charge transfer ability is not fully understood, although work on such systems has increased recently.[24] Truly, functional molecular electronics require the ability to transfer charge in more than two directions, and understanding charge transport in two directions is a step toward designing functional molecular transistors. An ideal molecular bridge would have a maximum rate of charge separation (CS) to form a charge transfer (CT) state and would resist the charge recombination (CR) relaxation process to the ground state. Furthermore, the molecular bridge would be used to control the transport of charge through a molecular device.

In cross-conjugated molecules, two unsaturated groups are conjugated to a third unsaturated group but are not conjugated to each other.[25] Cross-conjugation can be found in many types of organic molecules, but the study of CT in these molecules is relatively uncommon.[12,26–28] Recent interest in these molecules stems from the apparent ability to control the transfer of charge through the molecules as would be necessary in molecular electronics.[29–33] In some cases, cross-conjugated molecules have been shown to be effective at transferring charge despite reduced conjugation and have also been shown to allow for effective CS with slow CR rates.[28,34–36] In a study by Thompson et al., which utilized linearly or cross-conjugated phenylacetylene bridges, CS times were shown to be faster, while the CR rates were shown to be slower in molecules containing cross-conjugated bridging groups.[28] In a study by Ricks et al., CS occurred slower in a DBA molecule with a cross-conjugated 1,1-diphenylethene bridge than in its linearly conjugated counterpart with a *trans*-stilbene bridge.[12] It would appear as though the rates of CS and CR are dependent on the molecules in which the processes are occurring, but more work needs to be conducted on CS and

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CR times in cross-conjugated molecules to determine the variables that account for such observations.

In this work, we will explore the effect of conjugation on the rate of CS and CR in cross-conjugated molecules containing m-phenylene (mP) bridges and in linearly conjugated molecules containing 2,5-thiophene (Th) bridges. The donor, a veratrole group, and acceptor, a phthalimide group, are separated by either one (acyclic) or two (macrocyclic) bridging units. The macrocycles possess greater rigidity allowing for excellent π-overlap and provide a second conjugation pathway accessible for CT.

The synthesis of the asymmetric acyclic molecules D(mP)A and D(Th)A, the cyclic analogs, $D(mP)_2A$ and $D(Th)_2A$, and the symmetric cyclic analogs $A(mP)_2A$, $D(mP)_2D$, $A(Th)_2A$, and $D(Th)_2D$ (Chart 1) was recently reported.[34] In that study, preliminary characterization was conducted primarily by steady-state UV–Vis and fluorescence spectroscopy.[34] From that work, Lippert–Mataga plots were constructed for each DBA compound. The results of the study showed that $D(mP)_2A$, D(mP)A, and D(Th)A fluoresced from CT states in solvents more polar than cyclohexane. In contrast, $D(Th)_2A$ was found to fluoresce from a nonpolar locally excited (LE) state in cyclohexane, toluene, and dioxane, and from a CT state in more polar solvents such as chloroform and dichloromethane (DCM).[34] UV–Vis spectra of the DBA compounds were found to have no solvatochromism in solvents of varying polarity. Additionally, the UV–Vis spectra of the DBA compounds were not redshifted relative to their symmetrical analogs. These findings support the idea that the LE state is initially populated in all DBA compounds as opposed to direct excitation into the CT state. It should be noted that the LE state can be emissive. For instance, an LE band was observed in the steady-state emission of D(mP)A in chloroform and DCM at ~400 nm. In fact, in chloroform, the LE state and CT state were observed simultaneously in D(mP)A. The CT state had an emission maximum of ~600 nm.[34]

Here, we use femtosecond transient absorption (TA) and time-correlated single photon counting (TCSPC) to study the relaxation pathways, CS, and CR rates in several compounds in polar solvent and a nonpolar solvent to gain insight into the ICT process. TA and TCSPC are complementary time-resolved techniques. TCSPC allows for determination of emissive state lifetimes while TA allows for determination of lifetimes associated with both radiative and nonradiative decay processes from the excited state. When similar lifetimes are observed in TA and TCSPC, we can assume that the TA spectra have contribution from an emissive state. In many cases, TA spectra are must be fit to multi-exponential decays. In these instances, it is likely that more than one photophysical or photochemical process, which may be radiative or nonradiative, is taking place in the excited state.

Intramolecular charge transfer has been shown to be dependent on solvent polarity.[37–40] Specifically, a redshift in fluorescence maxima occurs with an increase in solvent polarity due to the increased stability of the polar CT state in a polar medium in accordance with the Lippert equation. Therefore, formation of the CT state in a polar solvent, such as DCM, should be energetically favorable, and the CT state is expected to be longer lived than in nonpolar solvents such as toluene. Like DBA molecules with linearly conjugated bridges, the trend of redshifting spectra with an increase in solvent polarity has been shown to hold true in a cross-conjugated system with bis-substituted pyridylvinylene derivatives.[41]

Comparison of cross-conjugated bridging groups to the linearly conjugated bridging groups in each solvent will allow for better understanding of the effect of bonding on the associated decay processes from the excited states, including CS and CR. The addition of a second bridge to form a macrocycle will allow for the exploration of the rate of CS and CR in molecules, which possess 2-D conjugation. The symmetric analogs allow for comparison between molecules capable of CT from donor to acceptor and those that are not. Observation of the TA spectra and dynamics in the compounds used in this study will provide understanding of the available LE and CT states and to any possible geometry changes. Herein, we explore the solvent effect on excited-state properties of the aforementioned compounds via observation of their TA spectra and kinetics. We report the first known femtosecond TA spectra and dynamics of a cross-conjugated macrocycle with multiple conjugation pathways.

EXPERIMENTAL

The laser system used in the TA experiments is housed in the Center for Chemical and Biophysical Dynamics at The Ohio State University and has been described previously.[42] Briefly, a Ti : Sapphire oscillator and regenerative amplifier (Coherent, Santa Clara, CA) generate 2.4 mJ, 50 fs pulses centered at 800 nm with a repetition rate of 1 kHz. The main portion of the fundamental pumps an optical parametric amplifier (OPA). The OPA allows for the wavelength of the pump to be adjusted for the molecule of interest. For this work, 310 nm light was generated in the UV/Vis OPA for use as the pump as this was in the absorption band of each of the molecules. The second portion of the fundamental provides the white light for the broadband experiments. This beam is split using the front and back reflection from a 6 mm CaF_2 window to generate the probe and reference beams. The pump beam is overlapped only with the probe beam. A polarizer was placed in the path of the probe beam after the sample to reduce emission from the sample from reaching the detector.[43,44] A flowing sample cell with a 1-mm path length was used to ensure fresh sample was being photoexcited. Broadband spectra were collected on a thermoelectrically cooled CCD detector. The broadband experimental setup has been described previously.[45] The samples used in the TA experiments were not degassed. Broadband TA spectra were corrected for group velocity dispersion based on the two photon absorption spectrum of methanol.[46] Narrow peaks present at 620 nm are due to second order diffraction of the 310 nm pump pulse. The time resolution of the instrument is about 300 fs. Kinetic traces were constructed from the broadband spectra by plotting intensity at a particular wavelength over time.

The synthesis of the cross-conjugated (mP) and linearly conjugated (Th) symmetric and asymmetric compounds has previously been reported.[34] Samples used in the ultrafast laser experiments had a steady-state absorbance at the excitation wavelength ranging from 0.3 to 1 a.u. in a 1 mm quartz cuvette. Spectroscopic grade toluene and DCM were used without further purification. No sample degradation was found by comparison of the steady-state absorption spectrum taken before and after the ultrafast laser experiment.

Kinetic traces were fit with a convolution of a Gaussian function representing the instrument response function (IRF), an appropriate number of exponentials, and an offset, if necessary. Time constants are given with an error of $\pm 1\sigma$. Decay-associated spectra (DAS) were constructed from decay traces collected every 10 nm along the TA spectrum. The decay traces were globally fit to a convolution of the IRF with two exponentials and an offset. The amplitudes associated with the exponentials and offset are then plotted against wavelength. The DAS provide insight to and spectra of the excited-state species responsible for components of the TA spectra at specific decay times.

Steady-state absorption spectra were collected on an absorption spectrophotometer using a 1 cm quartz cuvette. Steady-state emission spectra were collected with 350 nm excitation and a 2 nm or 3 nm slit width. Spectra were corrected for detector response. Samples were prepared in

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spectrophotometric grade solvents without further purification and were nitrogen purged for the emission experiments. The solvent contribution was subtracted from both the steady-state absorption and emission spectra.

Fluorescence lifetimes were collected using the Horiba Jobin Yvon Fluoromax-4 with the TCSPC accessory. The samples were excited with a 310-nm diode laser with an IRF of ~1.3 ns. An aqueous solution of nondairy coffee creamer was used as the scattering solution to obtain the IRF. Emission lifetime decay traces were fit to a numerical convolution of one or two exponential functions and the IRF.[47]

RESULTS

Each of the symmetric and asymmetric linear and cross-conjugated compounds was explored using femtosecond TA spectroscopy and TCSPC in toluene and DCM (Fig. 1). These two solvents were chosen to explore the effect of solvent polarity on CT ability. The results in the succeeding text are grouped by type of compound. All kinetic traces and some figures containing TA spectra of some compounds can be found in the Supplemental Information. A summary of the fluorescence and TA lifetimes is given in Table 1. CS and CR times for the DBA compounds in DCM and toluene are summarized in Tables 2 and 3, respectively. The steady-state absorption and emission spectra of each DBA compound in toluene and DCM are shown in Fig. 2. Steady-state absorption and emission of the symmetric compounds can be found in the Supplemental Information.

In the femtosecond TA experiments, 310-nm excitation is used. At this wavelength, the donor molecule has a small molar absorptivity. Therefore, it is the acceptor portion of the molecule that becomes excited. Emission from the LE state results from radiative relaxation of the acceptor portion of the molecule.
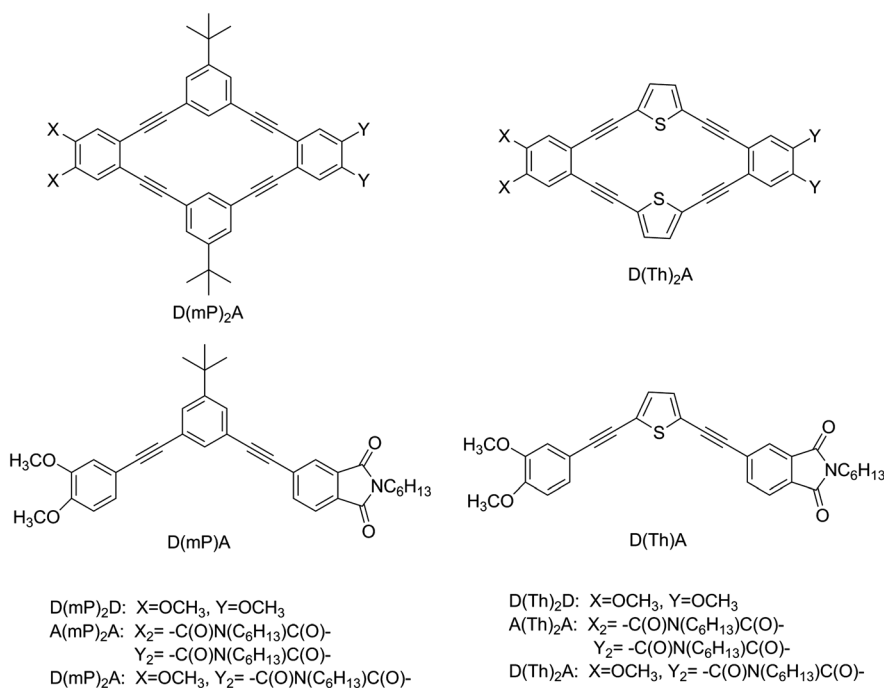
at 433 nm and the other above 650 nm) in about 20 ps. An isosbestic point is observed at 600 nm suggesting a transition from the initially populated LE state to the CT state. Once formed, the resulting peaks appear to decay simultaneously in 1.0 ± 0.1 ns (Figs. S1 and S2).

In toluene, a broad band is formed upon excitation which then decays within ~1 ps to form a band with vibronic structure whose maximum is at 481 nm (Fig. 3b). This band subsequently blueshifts within about 10 ps to form a band with vibronic structure whose maximum is at 437 nm. The blueshift and the associated time constant are consistent with vibrational cooling.[48–51] After vibrational cooling, the 437 nm band is long lived and does not decay significantly within the time duration of the experiment (Fig. S3).

The fluorescence lifetime of D(mP)A in toluene was determined to be double exponential with time constants of 2.16 ± 0.02 ns and 17.85 ± 0.06 ns. The apparent long-lived state observed via the TA spectra in toluene likely results from the same state as the state observed in the emission experiments, which was previously assigned to be a CT state.[34] In DCM, the fluorescence lifetime of D(mP)A was determined to be 0.57 ± 0.01 ns, which represents the decay of the CT state. It should be noted that this observed lifetime was within the IRF of the excitation source. In DCM, the CT state is accessed within 20 ps as evidenced by the picosecond decay component and isosbestic point in the TA spectra. Also from the TA spectra, the CR time was determined to be 1.0 ± 0.1 ns. We attribute this time constant to be the result of decay from the emissive state. The small discrepancy in the time constants observed in the TA and the fluorescence lifetime experiments likely arises from the similarity of the time constant to the IRF in the fluorescence experiments.

Transient absorption spectra of the acyclic asymmetric cross-conjugated compound

The TA spectrum of D(mP)A in DCM (Fig. 3a) initially has a broad band that decays to form a TA spectrum with two maxima (one

Transient absorption spectra of the cyclic asymmetric cross-conjugated compound

In the TA spectra of D(mP)$_2$A in DCM (Fig. 4(a) and (b)), we observe a broad band with a maximum at 481 nm and another peak at 357 nm. The peak at 357 nm blueshifts to a wavelength less than 350 nm (outside of the detection window) within a few tens of picoseconds and decays but not completely within the time duration of the experiment. An isosbestic point at 422 nm is observed in the early time spectra (up to 2 ps) suggesting a transition between excited states. Neither the band at 481 nm nor the band at 350 nm decays completely within the time duration of the experiment (Fig. S4). However, it is likely that the lifetime is less than 3 ns given the general trend of the decay of the band. The fluorescence lifetime of D(mP)$_2$A in DCM was determined to be 2.39 ± 0.01 ns in degassed solution. It was determined previously that the emission lifetime arises from a CT state.[34] Because of the similar lifetimes measured in the TCSPC and projected in the TA experiments, we suggest that the TA spectrum arises from the same CT state as observed in the previous emission experiments. The isosbestic point suggests that the LE state is initially populated, but within 2 ps, the

D(mP)$_2$A

D(Th)$_2$A

D(mP)A

D(Th)A

D(mP)$_2$D: X=OCH$_3$, Y=OCH$_3$
A(mP)$_2$A: X$_2$= -C(O)N(C$_6$H$_{13}$)C(O)-
              Y$_2$= -C(O)N(C$_6$H$_{13}$)C(O)-
D(mP)$_2$A: X=OCH$_3$, Y$_2$= -C(O)N(C$_6$H$_{13}$)C(O)-

D(Th)$_2$D: X=OCH$_3$, Y=OCH$_3$
A(Th)$_2$A: X$_2$= -C(O)N(C$_6$H$_{13}$)C(O)-
              Y$_2$= -C(O)N(C$_6$H$_{13}$)C(O)-
D(Th)$_2$A: X=OCH$_3$, Y$_2$= -C(O)N(C$_6$H$_{13}$)C(O)-

Figure 1. Structures of D(mP)$_2$A, D(Th)$_2$A, D(mP)A, D(Th)A and their symmetric counterparts

Table 1. Fluorescence and transient absorption lifetimes in various solvents

	Solvent[a]	τ_f (ns)	τ_{TA}
D(Th)$_2$D	Tol	1.255 ± 0.002	4 ± 1 ps (rise), 1.9 ± 0.4 ns (decay)
	DCM	—	5 ± 1 ps (rise), 1.3 ± 0.1 ns (decay)
A(Th)$_2$A	Tol	2.1	—
	DCM	—	8 ± 2 ps (rise), 4 ± 2 ns (decay)
D(mP)$_2$D	Tol	3.705 ± 0.003	>2.5 ns (decay)
	DCM	—	>2.5 ns (decay)
A(mP)$_2$A	Tol	5.907 ± 0.005	>2.5 ns (decay)
	DCM	—	>2.5 ns (decay)
D(mP)A	Tol	2.16 ± 0.02, 17.85 ± 0.06	~1 ps (decay), ~10 ps (blueshift), >2.5 ns (decay)
	DCM	0.57 ± 0.01[a]	~20 ps (decay), 1.0 ± 0.1 ns (decay)
D(mP)$_2$A	Tol	18.48 ± 0.01	4 ps decay (410 nm), >2.5 ns
	DCM	5.0	~10 s of ps (blue shift), >2.5 ns (decay)
D(Th)A	Tol	0.38 ± 0.01[a]	>2.5 ns (decay)
	DCM	0.62[b]	~10 ps (blue shift), 1.0 ± 0.3 ns (decay)
D(Th)$_2$A	Tol	Within IRF	6 ± 1 ps (rise), >2.5 ns (decay)
	DCM	1.0[b]	2 ± 2 ps (rise), 1.0 ± 0.2 ns (decay)

DCM = dichloromethane, Tol = toluene.
[a]Within the instrument response function (IRF).
[b]From Ref. [34].

Table 2. Charge separation and charge recombination times for asymmetric cross-conjugated and linearly conjugated compounds in dichloromethane

	τ_{CS}	τ_{CR}
D(mP)A	~20 ps	1.0 ± 0.1 ns
D(mP)$_2$A	~2 ps	2.39 ± 0.01 ns
D(Th)A	Within 10 ps	1.0 ± 0.3 ns
D(Th)$_2$A	Within 2 ps	1.0 ± 0.2 ns

Table 3. Charge separation and charge recombination times for asymmetric cross-conjugated and linearly conjugated compounds in toluene

	τ_{CS}	τ_{CR}
D(mP)A	~1 ps	>2.5 ns
D(mP)$_2$A	~4 ps	>2.5 ns
D(Th)A	Within IRF	>2.5 ns
D(Th)$_2$A	Within IRF	>2.5 ns

IRF, instrument response function.

CT state becomes populated. The decay of the CT state results in CR on the nanosecond timescale.

Upon excitation, D(mP)$_2$A in toluene displays a broad TA band with a peak at 480 nm and a shoulder at 413 nm (Fig. 4(c)). The shoulder decays with a time constant of 4 ± 1 ps. We believe that this shoulder represents decay from the initially populated LE state to the CT state. After about 10 ps, another shoulder with a maximum of about 370 nm becomes apparent. Its intensity increases throughout the time duration of the experiment. The lack of observable decay in the TA spectra on the timescale of this experiment suggests the TA band could have a rate of decay similar to what was observed in the TCSPC experiment. This suggests that the TA band may result from decay of the same state as observed in the fluorescence experiments: the CT state.[34] The TA shows very little decay in the time duration of the experiment possibly signifying a photoproduct, although a triplet state cannot be ruled out. The TCSPC experiments gave an emission lifetime of 18.48 ± 0.01 ns for D(mP)$_2$A in degassed toluene solution.

Transient absorption spectra of the acyclic asymmetric linearly conjugated compound

Upon excitation in DCM, D(Th)A has a maximum at ~620 nm at early times, but then, blue shifts to 600 nm within 10 ps (Fig. 5(a)). This is likely the result of vibrational cooling.[50] The band subsequently decays to the baseline in 1.0 ± 0.3 ns (Fig. S8). This lifetime is somewhat longer than that observed in the fluorescence lifetime experiments in which the lifetime was found to be 0.62 ns.[34] The previously constructed Lippert–Mataga plots suggest that the emitting state is the CT state.[34] It is likely that the TA band arises from the CT state because of the similar time constants.

In toluene, D(Th)A initially shows a stimulated emission band that is formed with a maximum at 467 nm (Fig. 5(b)). The previously obtained steady-state emission spectrum of D(Th)A in toluene has a maximum at 480 nm and is believed to arise from a CT state.[34] Because of the similar wavelength maxima of the steady-state emission and the stimulated emission, the observed stimulated emission is likely due to CT. Strong overlap of the stimulated emission band with a TA band with a maximum at 640 nm likely distorts the maximum of the stimulated emission band from its steady-state maximum.

The stimulated emission band at 467 nm is overcome by absorption to form a broad band with absorption from 400–662 nm (This most likely extends further into the red,
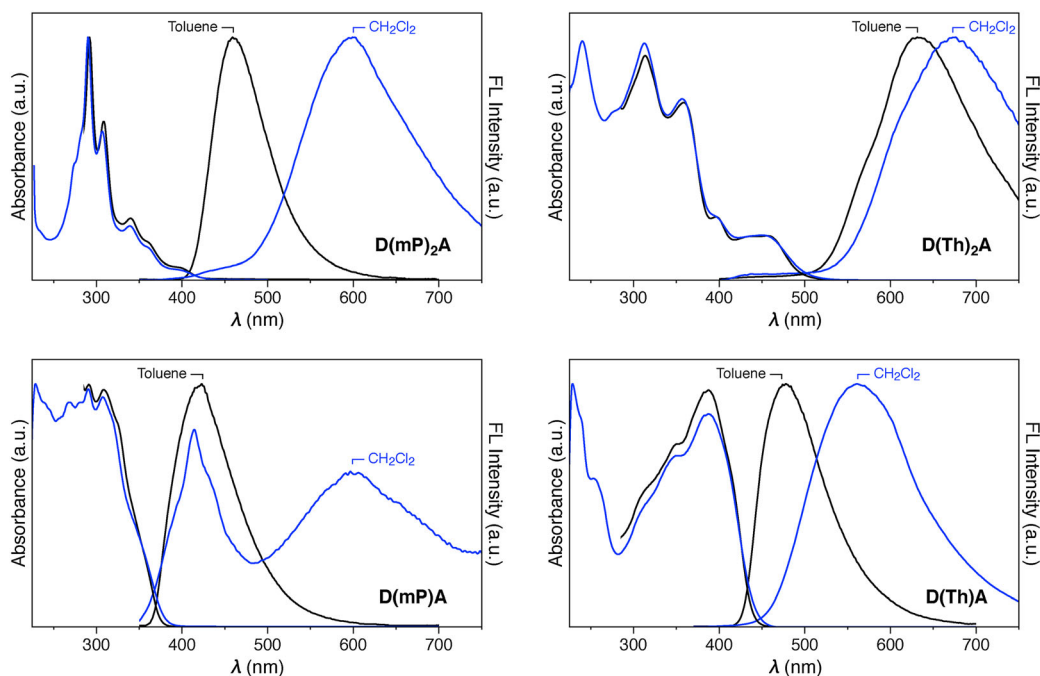
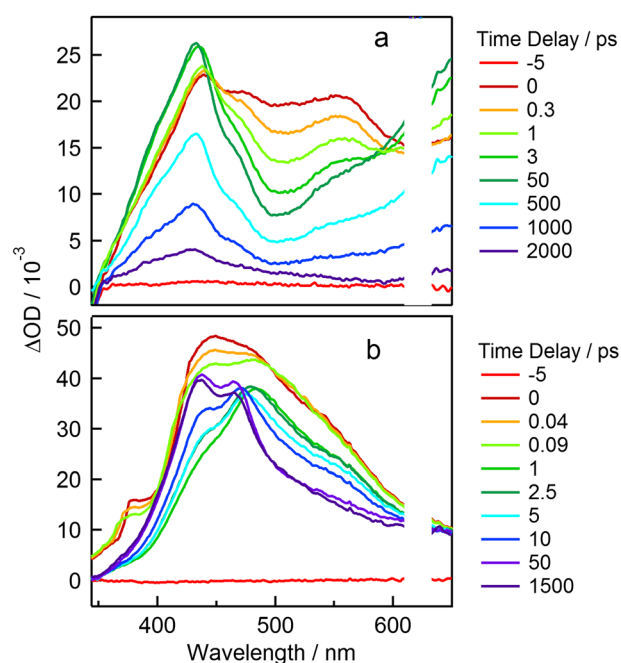**Figure 2.** Absorption and emission spectra of asymmetric compounds in toluene (black) and DCM (blue)[34]

to the TA band, are populated simultaneously and within the IRF. This gives rise to a long-lived mixed state whose character consists of contributions from the CT state and a long-lived dark state. Mixed states have been shown to stabilize an otherwise meta-stable state to yield a long lifetime.[52–54]
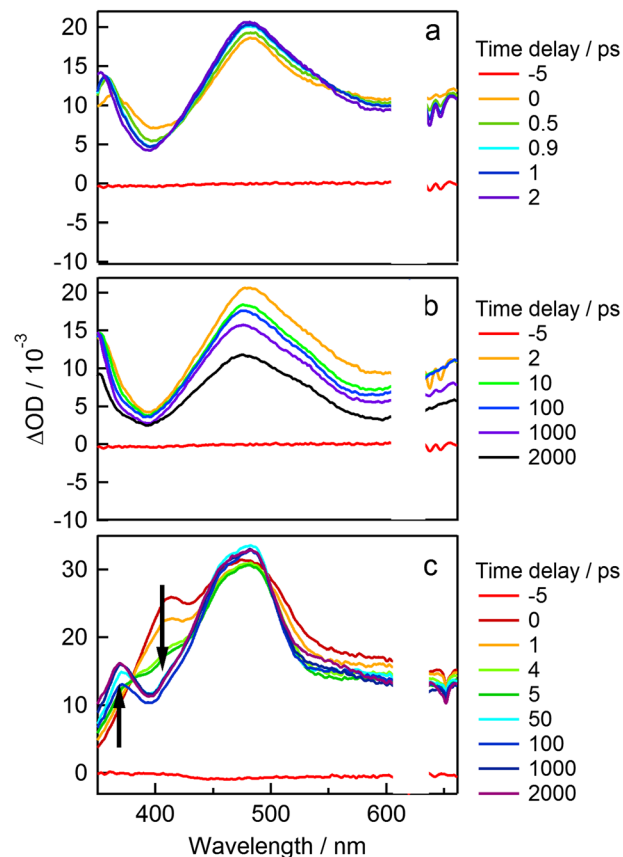
Transient absorption spectra of the cyclic asymmetric linearly conjugated compound

The TA spectra of D(Th)$_2$A in toluene and DCM have a similar spectral shape (Figs. 6 and 7). In toluene, the band maximum is at 516 nm, and in DCM, the maximum is at 518 nm. The bands in both solvents
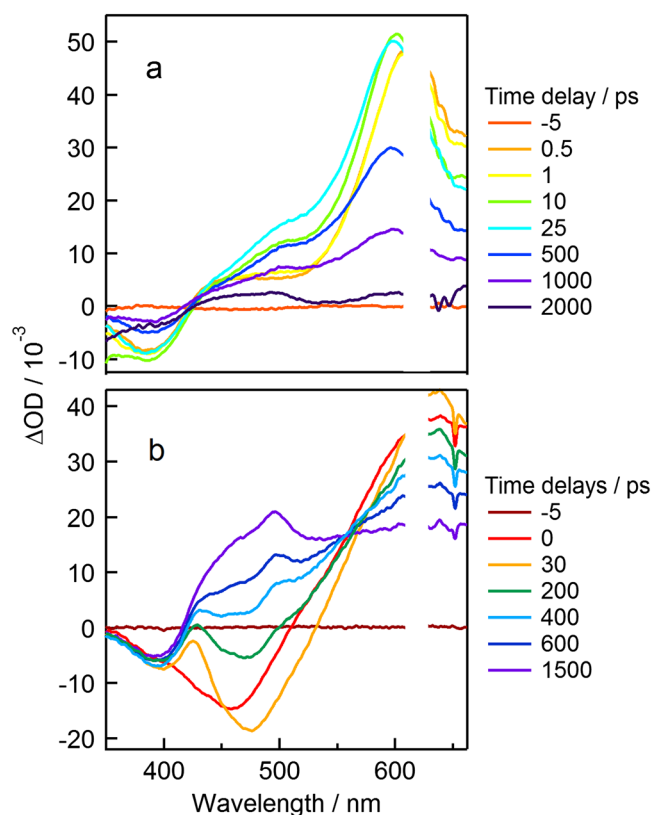
but the limit on the spectrometer was about 662 nm). This band does not decay within the time duration of the experiment as shown in Fig. S6. The time constant associated with the recovery of the stimulated emission band cannot be determined other than to say it occurs on the picosecond timescale given the overlap of a strong TA band as shown in Fig. S7. The emission lifetime of D(Th)A in toluene was unable to be obtained as it was within the IRF of ~1.4 ns. It was determined previously that emission is from the CT state.[34] We suggest that in toluene, both the CT state, which gives rise to the stimulated emission, and a long-lived dark state, which gives rise

show a rise time. In toluene, the rise time is 6 ± 1 ps (Fig. 6(a)) while in DCM, the rise time is 2 ± 2 ps (spectra were somewhat noisy) as shown in Fig. 7(a). The observed rise time in the TA band
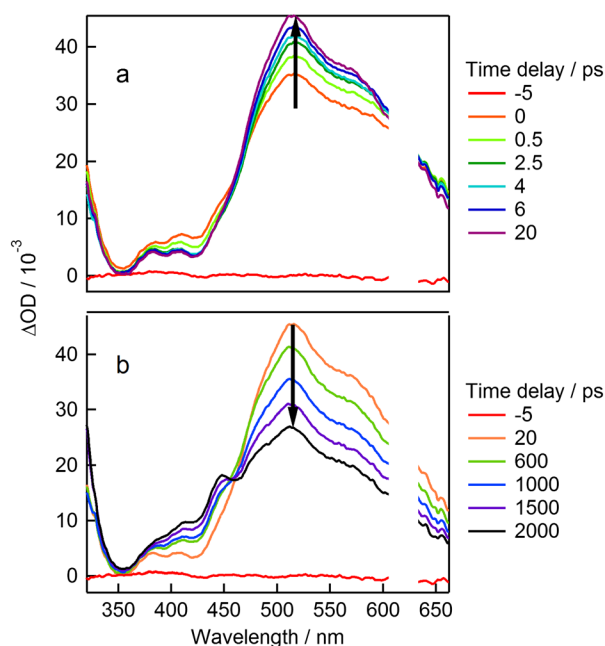

Figure 3. TA spectra of D(mP)A in DCM (a) and toluene (b)

Figure 4. TA spectra of D(mP)$_2$A in DCM at early times (a) and later times (b) and in toluene (c)
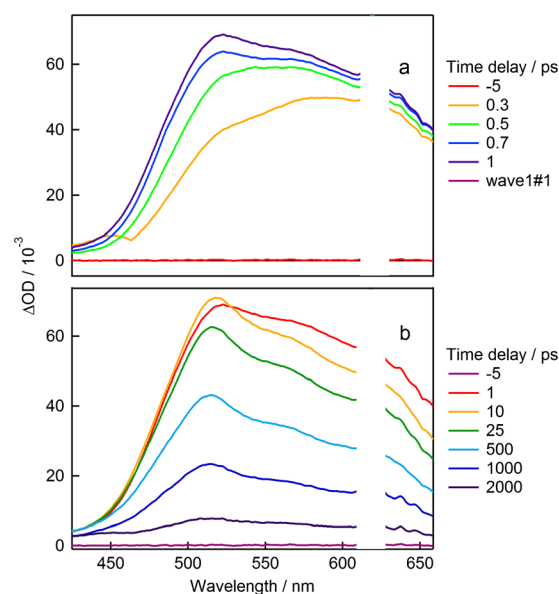
Figure 5. TA spectra of D(Th)A in DCM (a) and toluene (b)

Figure 6. TA spectra of D(Th)₂A in toluene at early times (a) and later times (b)

Figure 7. TA spectra of D(Th)₂A in DCM at early times (a) and later times (b)

is consistent with the emission lifetime of 1.0 ns suggesting that the TA band results from the same state as the emissive state, the CT state.[34] Construction of Lippert–Mataga plots in previous work has suggested that D(Th)₂A emits from the CT state in DCM and a LE state in toluene.[34]

The TA lifetime of D(Th)₂A in toluene is longer lived than in DCM. The fluorescence lifetime in toluene is within the IRF of 1.4 ns. In the 2 ns time duration of the TA experiment, the TA band in toluene decays by about 55% owing to a decay time longer than 2.0 ns (Figs. 6(b) and S10). Unlike in DCM, D(Th)₂A in toluene has an isosbestic point at 464 nm. This suggests that two states are contributing to the TA spectrum. It is possible that mixing of a dark state and emissive CT states gives rise to this isosbestic point and attributes to the longer lifetime in toluene.[52–54]

Transient absorption spectra of symmetric linearly conjugated compounds

Upon excitation of D(Th)₂D in toluene, a band with a maximum around 560 nm is formed with a 4 ± 1 ps rise time and decays in 1.9 ± 0.4 ns (Figs. S11 and S12). As the band at 560 nm decays, a narrow band at 424 nm becomes visible after about 200 ps. The intensity of this band continues to increase throughout the duration of the experiment. It is likely that this band arises from the formation of a transient photoproduct (as no changes were observed in the steady-state absorption spectra before and after the TA experiment).[55] Because of the overlap of the band at 560 nm with the band at 424 nm, it is difficult to obtain a reasonable rise time for the 424 nm band.

D(Th)₂D in DCM (Figs. S13 and S14) is very similar to that in toluene. Upon excitation, a band at 552 nm is formed in the TA spectrum with a rise time of 5 ± 1 ps. It decays with a time constant of 1.3 ± 0.1 ns. As this band decays, a band with a maximum at 422 nm rises. It becomes apparent after about 100 ps and continues to rise throughout the time duration of the experiment. As in toluene, it is likely this is the result of a transient photoproduct. The wavelength maxima of the bands formed in the blue region do not appear to be solvent dependent. The

likely corresponds to a geometric rearrangement in the excited state. Similar observations of rise times in the symmetric compounds were made and attributed to geometric rearrangement as discussed in the succeeding text. The TA band of D(Th)₂A in DCM decays with a time constant of 1.0 ± 0.2 ns (Figs. 7 and S9), which

TA lifetimes of D(Th)$_2$D in DCM and toluene are the same within error, which suggests that very little solvent dependence is observed in these compounds. This is consistent with an excited state that has no CT character as is expected for the symmetric compounds. The previously measured fluorescence lifetime for D(Th)$_2$D in cyclohexane is 1.1 ns.[34] Because of the similar time constants, it is likely that the band formed after the rise time in toluene and DCM results from the fluorescing state, which has previously been assigned to the nonpolar LE state.

A(Th)$_2$A in DCM (Figs. S15 and S16) behaves similarly to D(Th)$_2$D in DCM. Upon excitation, a band at 560 nm is formed. It has a rise time of 8 ± 2 ps and decays with a time constant of 4 ± 2 ns (the error in this time constant is large because the band did not fully decay within the time duration of the experiment). A band at 446 nm with a shoulder at approximately 418 nm begins to form during the experiment and becomes apparent after about 400 ps. The decay time of the 560 nm band is similar (within error) to the time constant previously determined for the fluorescence lifetime in toluene of 2.1 ns and has been determined to arise from the nonpolar LE state.[34] Because of the similar lifetimes, it is likely that the TA band arises from the same LE state. As in D(Th)$_2$D, the band at 446 nm likely arises from a transient photoproduct. Again, it is difficult to obtain a rise time for the band attributed to the photoproduct because of the overlap between it and the band at 560 nm.

Transient absorption spectra of symmetric cross-conjugated compounds

D(mP)$_2$D and A(mP)$_2$A in both solvents have very broad spectra from 380 nm to the red edge of the detection limit. The TA spectra of A(mP)$_2$A in DCM show two peaks (Fig. S17). For D(mP)$_2$D, the bands are at 418 and 578 nm in toluene and at 410 and 567 nm in DCM (Figs. S18 and S19). For A(mP)$_2$A in toluene, the bands are located at 422 and 557 nm (Fig. S20) while in DCM, the bands are at 425 and 534 nm.

The TA spectra of these compounds showed little to no decay over the time duration (~2.5 ns) of the experiment suggesting long TA lifetimes similar to those found via fluorescence experiments. The previously recorded fluorescence lifetimes of D(mP)$_2$D and A(mP)$_2$A in cyclohexane were found to be 3.3 and 5.5 ns, respectively. For A(mP)$_2$A in toluene, there is a 15% decrease in the intensity of the band over the 2.5 ns duration of the experiment. For the same compound in DCM, the decrease is negligible. D(mP)$_2$D in toluene decays approximately 30% throughout the time duration of the TA experiment, and in DCM, the band decays approximately 20%. These long lifetimes suggest that the observed TA bands are due to the same state as the nanosecond-lived emitting state, which has previously been suggested to be the nonpolar LE state.[34] As there are no rise times associated with the low and high energy TA bands, it is likely that the compounds are excited directly into the LE state from which they then decay on the nanosecond timescale. Furthermore, the low and high energy bands decay simultaneously suggesting they arise from the same state.

DISCUSSION

Geometry changes

The observed rise times in the compounds containing two bridging Th groups likely result from a geometry rearrangement in the excited state. Leu *et al.* have previously determined that the thiophene rings are twisted 42° from the plane of the molecule in the ground state in the macrocycles based on density functional theory calculations.[34] Photoexcitation has been shown to cause a flattening of linearly conjugated molecules in the excited state and results in a picosecond time constant.[56–58]

Decay-associated spectra

For those compounds with the cross-conjugated mP bridging units, formation of the CS state occurs on the picosecond time scale as is evidenced by the spectral changes observed in D(mP)$_2$A and D(mP)A in both solvents. This CS rate constant in D(mP)$_2$A and D(mP)A in both solvents is attributable to the transition from the DBA* (LE) to the D$^+$BA$^-$ (charge separated) state. DAS were constructed for both compounds in DCM in which we observe an initially populated LE state followed by decay to the CT state and are shown in Figs. 8 and S21. For D(mP)$_2$A (Fig. 8), the picosecond component of the fit has an absorption maximum centered around 585 nm. At this wavelength, the nanosecond component has much lower intensity. The nanosecond component has maxima at 480 and 360 nm. At these wavelengths, the picosecond component has negative amplitudes. This suggests that the species that exists on the picosecond timescale evolves into the species that exists at the nanosecond timescale. The DAS of the picosecond species correspond to the spectrum of the DBA* species of D(mP)$_2$A in DCM while the DAS of the nanosecond species correspond to the spectrum of the D$^+$BA$^-$ species of D(mP)$_2$A.

The DAS of the picosecond component for D(mP)A in DCM (Fig. S21) has a maximum around 520 nm. The nanosecond component has a maximum at 430 nm and another to the red of 650 nm. As in D(mP)$_2$A, the picosecond component has negative amplitudes at the wavelengths at which the nanosecond component has maxima suggesting that the DBA* species that exists during the picosecond timescale evolves into the D$^+$BA$^-$ species that exists on the nanosecond timescale.

Rates of charge separation and charge recombination

As mentioned previously, the rate of CS in cross-conjugated molecules has been shown to be faster in one study and slower in another compared with linearly conjugated analogs.[12,28] In the results presented here, CS occurs on the picosecond timescale in each of the cross-conjugated compounds in both DCM and toluene as shown in Tables 2 and 3, respectively. Specifically,
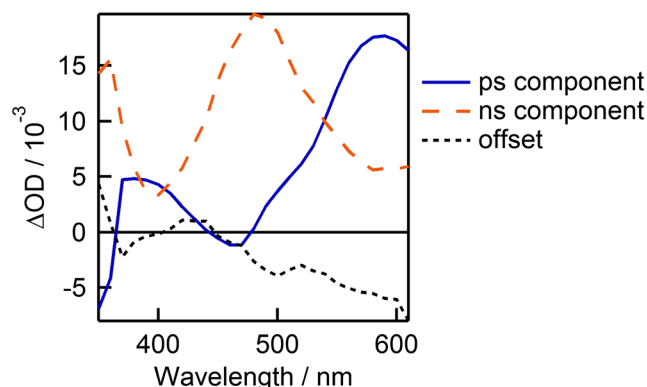

Figure 8. DAS of D(mP)$_2$A in DCM

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CS occurs in about 20 ps in D(mP)A and about 2 ps in D(mP)$_2$A in DCM and in about 1 and 4 ps, respectively, in toluene. The linearly conjugated cyclic compounds do not show rise times or spectral changes that can be attributed to CS. Therefore, in the linearly conjugated compounds, it is proposed that CS occurs within the instrument response time or that the CT state is accessed immediately upon excitation. However, because of the limitations of our experiment, we can only be sure that CS occurs within 2 ps in D(Th)$_2$A and 10 ps in D(Th)A in DCM and within the IRF in toluene. Given these time constants, CS must be slower in the cross-conjugated compounds than the linearly conjugated counterparts we studied. This observation is somewhat expected as cross-conjugation is expected to limit electronic communication across the molecule due to the decreased orbital overlap.

Addition of a second cross-conjugated bridge to form the cyclic compound, D(mP)$_2$A, allows for a faster CS rate in comparison with the acyclic compound, D(mP)A. The added structural rigidity in the cyclic compound likely aids in formation of the CS state because it increases π-overlap between the donor and bridging portion of the compound. Because of the increase in π-overlap, the rate in which charge can be transferred is faster.

Charge recombination in D(mP)$_2$A is about twice as long in polar solvents compared with that of D(mp)A. This suggests that the cyclic compound has better CS than the acyclic compound. One possibility for the slower CR rates in these compounds could be due to the added conformational stability given by the second bridging unit, which likely reduces the availability of the deactivation pathway. A second possibility could arise from the reduced electronic coupling between the CT state and ground state. If we consider a simple two-state charge recombination model and neglect any role the LE state may play, we can see that the CR process is dependent on the magnitude of the transition dipole moment, M_v, between the CT and ground states.[52] In turn, M_v is dependent upon the change in dipole moment for the transition, $\Delta\mu$, the energy of the transition, $h\nu$, and the electronic coupling matrix element between the CT and ground states, V, as given by the equation $M_v = (V\Delta\mu)/(h\nu)$. Furthermore, for a large M_v, the transition moment should be directed along the axis of CT.[53,54] Previous time-dependent density functional theory calculations on the macrocyclic compounds showed the highest occupied molecular orbital–lowest unoccupied molecular orbital transition moment to be polarized orthogonal to the axis of CT due to the symmetries of the excited and ground states.[34] As a result, relaxation via CR is symmetry forbidden leading to a slower rate of CR. The excited-state spectra observed for the DBA compounds in toluene did not return to the ground state within the time duration of the experiment, so a statement cannot be made on the CR rates.

In the two studies mentioned previously that observed CS and CR in cross-conjugated compounds, Thompson *et al.* reported CR times of 16.8 ns for the cross-conjugated compound they studied while the linearly conjugated analog had a CR time of 1.8 ns.[28] Ricks *et al.* reported a CR time of over 1000 ns for a cross-conjugated compound while its linearly conjugated analog had a CR time of a mere 107 ± 5 ns.[12] While there is great variation in the CR times for the various molecules studied, it is clear that CR times are consistently longer in cross-conjugated compounds than in linearly conjugated compounds. The same holds true for the compounds studied in this work in DCM. The cross-conjugated cyclic compound, D(mP)$_2$A, has nearly double the CR time of its linearly conjugated cyclic analog, D(Th)$_2$A.

Furthermore, although the CS time is slower in the cross-conjugated compounds than the linearly conjugated compounds studied here, it is still possible to get efficient CS and extended CR time compared with the linearly conjugated compounds making cross-conjugated compounds a viable option for molecular electronics.

Solvent dependence

In the DBA compounds, we observe highly solvent dependent dynamics. For the DBA compounds, the lifetime of the observed state in the TA spectra is longer in toluene than in DCM because of possible mixing of the CT and long-lived dark states in the nonpolar solvent in the compounds with Th bridges. In a polar solvent such as DCM, a polar excited state such as the CT state is stabilized resulting in greater energetic separation between the dark and CT states. The greater separation between the states does not allow for mixing as easily as it does in states that lie closely together energetically. Therefore, the majority of the population of excited molecules decays from the CT state, which is shorter lived than the dark state.

The cross-conjugated DBA compounds in DCM are initially excited into a LE state, but after a few picoseconds, the CT state is accessed as evidenced by the presence of isosbestic points. The linearly conjugated DBA compounds do not show isosbestic points in the TA spectra, and it is believe that the CT states are accessed on the picosecond time scale. There is no strong evidence for mixed states in DCM as there is in toluene.

Symmetric compounds

The TA lifetimes obtained for the symmetric compounds agree well with the previously obtained fluorescence lifetimes suggesting that the emitting state and observed TA states are the same. Generation of a photoproduct in the symmetric linearly conjugated compounds gives rise to a band, which increases in intensity throughout the duration of the experiments. The symmetric linearly conjugated compounds show a picosecond rise time that suggests a geometry change in the excited state.

CONCLUSIONS

We have observed TA and fluorescence spectra and measured lifetimes in various DBA compounds containing either cyclic or acyclic linearly conjugated or cross-conjugated bridges. We find that CS rates in DBA compounds with cross-conjugated bridges are slower than those of their linearly conjugated bridge counterparts. For the cross-conjugated compounds, extension of conjugation in two dimensions (macrocycles vs. acyclic) tends to decrease CS time by about a factor of ten and decreases the time of CR by a factor of about two in polar solvent. Nonpolar solvents allow for mixing of long-lived dark and CT excited states in the DBA compounds containing Th bridges while more polar solvents stabilize the CT state allowing for this state to be populated after a few picoseconds in cross-conjugated compounds. Our results present the first known femtosecond TA spectra and dynamics of cross-conjugated macrocycles with 2-D conjugation. The long CR times in the cross-conjugated macrocycles suggest the possibility of using such molecules in the design of molecular electronics.

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