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Dynamics of the Formation of a Charge Transfer State in 1,2-Bis(9-anthryl)acetylene in Polar Solvents: Symmetry Reduction with the Participation of an Intramolecular Torsional Coordinate

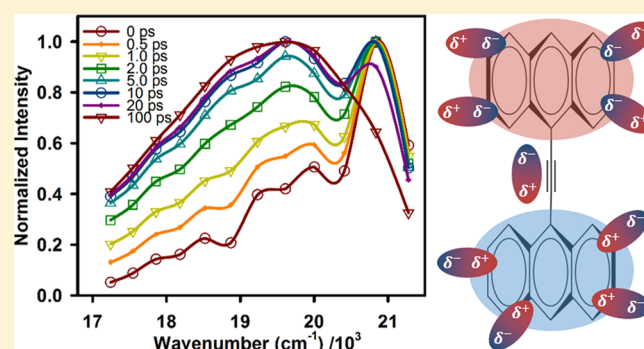
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S Supporting Information

ABSTRACT: We have studied 1,2-bis(9-anthryl)acetylene as a model compound for the characterization of the process of solvent-mediated symmetry reduction in an excited state. Thanks to the acetylenic bridge that joins the two anthracenic moieties, this system maintains minimal steric hindrance between the end chromophores in comparison with the classic 9,9'-bianthryl model compound. The acetylenic bridge also allows for significant electronic coupling across the molecule, which permits a redistribution of electron density after light absorption. Femtosecond resolved fluorescence measurements were used to determine the spectral evolution in acetonitrile and cyclohexane solutions. We observed that, for 1,2-bis(9-anthryl)acetylene, the formation of a charge transfer state occurs in a clear bimodal fashion with well separated time scales. Specifically, the evolution of the emission spectrum involves a first solvent-response mediated subpicosecond stage where the fluorescence changes from that typical of nonpolar solvents (locally excited) to an intermediate, partial charge transfer state. The second stage of the evolution into a full charge transfer state occurs with a much longer time constant of 37.3 ps. Since in this system the steric hindrance is minimized, this molecule can undergo much larger amplitude motions for the torsion between the two anthracenic moieties associated with the charge redistribution in comparison with the typical model compound 9,9'-bianthryl. Clearly, the larger range of motions of 1,2-bis(9-anthryl)acetylene gives the opportunity to study the electron transfer process with a good separation of the time scales for the formation of a partial charge transfer state, determined by the speed of solvent response, and the intramolecular changes associated with the formation of the fully equilibrated charge transfer state.



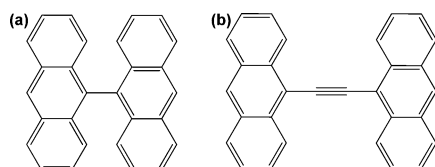
INTRODUCTION

Light induced separation of charges is one of the most fundamental processes in photochemistry and plays a central role in photosynthetic and photovoltaic applications.^{1–3} In the search for a fundamental understanding of this process, model symmetric systems like 9,9'-bianthryl (BA, see Scheme 1) have played a central role.^{4–13} In this kind of molecule, an initially formed electronically excited state (highly polarizable locally excited, nonpolar) can evolve toward a highly polar, charge

separated state where the solvent shells stabilize positive and negative charges localized respectively on the two anthracenic rings.^{9–11} This results in a bathochromic fluorescence shift due to the stabilization of the dipolar emissive state from the interaction with the polar solvent molecules.

The first time-resolved fluorescence experiments on BA suggested that the dynamics of the electron transfer reaction are governed mainly by solvation.^{7,8} More recent pump–probe studies have indicated that the excited state evolution occurs in two different stages, namely, locally excited (LE, nonpolar) → intermediate or partial charge transfer state (PCT) → fully relaxed charge transfer state (CT). The corresponding kinetic models for this process can include the possibility of the initial setup of an equilibrium between the LE and the intermediate PCT state.^{5,12–14} Such representation is based on BA's

Scheme 1. Structures of (a) 9,9'-Bianthryl (BA) and (b) 1,2-Bis(9-anthryl)acetylene (BisAA)



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emission spectrum evolution,¹³ transient absorption,^{6,14} and anisotropy measurements.¹² More specifically, in the transient absorption experiments by Kovalenko et al.,¹⁴ it was observed that although the spectral evolution is consistent with a two stage model (with a rapid initial equilibrium involving the LE state), *both* the first rapid stage and the latter stage are solvent controlled. That study assigned the sub 60 fs step in acetonitrile to a high frequency solvent coordinate, and the latter stage (subpicosecond in acetonitrile) to further solvent relaxation (diffusive or dissipative motions of the acetonitrile solvent shells). Importantly, the transient absorption experiments of Kovalenko et al.¹⁴ on BA do not distinguish evidence for the participation of an intramolecular torsional motion around the anthracene–anthracene single bridging bond related to the formation of the CT state. The use of BA as a model for charge transfer processes, therefore, does not permit a clear study of the role of intramolecular rearrangements which may be crucial and more general in CT dynamics (see below).

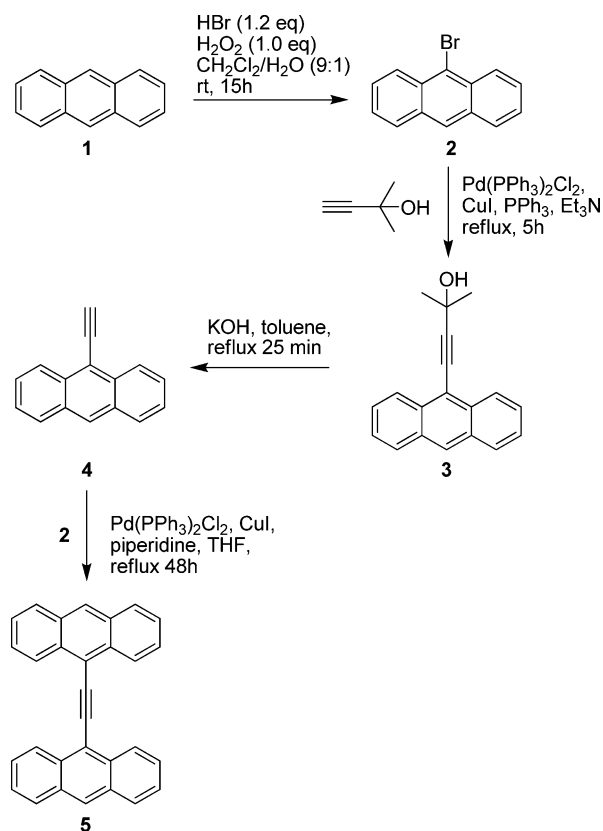
In this contribution we propose a new model compound for the study of the photoinduced symmetry reduction in polar solvents which can give much clearer information about the involvement of an intramolecular torsional coordinate. This compound, 1,2-bis(9-anthryl)acetylene (BisAA, see Scheme 1), maintains the fundamental properties of BA of a non-dipolar ground state due to the nuclear symmetry, and extended conjugation which allows for the charge transfer process. The BisAA molecule, however, has a much lower degree of restriction about its geometry in comparison with BA, where, due to the steric hindrance between the anthracenic units in BA (from the peri-hydrogens and their proximity), the ground state of this molecule has a perpendicular disposition between the two anthracenes (D_{2d} symmetry). In fact, from the hindrance, the electronically excited state of BA can evolve only within a minimal margin of conformations which by far cannot approach planar or near-planar geometries. This steric restriction in BA implies than any intramolecular geometric change is of minimal amplitude and therefore may occur (if at all) in time scales where the fast solvent motions are also occurring.

As mentioned, BisAA has a much more free range of motion for the inter-anthracene torsional coordinate, and also includes in the bridge an acetylenic triple bond which can accommodate these rotations.¹⁵ As we show through femtosecond fluorescence upconversion experiments, in this molecule we observed two well separated time scales for the formation of the CT state in acetonitrile. Since the slower stage is observed to occur in a widely different time scale from the fast one (most likely related to the solvent response), this system allows for the direct observation of the participation of an intramolecular torsional coordinate that can be included in advanced models for the charge transfer process.

EXPERIMENTAL SECTION

Methods and Materials. 1,2-Di(anthracen-9-yl)ethyne, also named 1,2-bis(9-anthryl)acetylene (BisAA (5)), was synthesized using the four steps presented in Scheme 2. Briefly, anthracene (1) was converted to 9-bromoanthracene (2) in the presence of aqueous hydrohalic acid and hydrogen peroxide following the bromination methodology reported by Vyas et al.¹⁶ Subsequently, reaction of 9-bromoanthracene with 2-methylbut-3-yn-2-ol in a standard Sonogashira coupling produced the corresponding 4-(anthracen-10-yl)-2-methylbut-3-yn-2-ol (3),^{9,17–20} which was converted to the 9-ethynylan-thracene (4)^{18,19} by treatment with potassium hydroxide in

Scheme 2. Synthesis of 1,2-Di(anthracen-9-yl)ethyne or 1,2-Bis(9-anthryl)acetylene (5)



refluxing toluene. Finally, the resulting terminal acetylene (4) was coupled with 9-bromoanthracene formed in the same coupling procedure used before to obtain (3), to yield the desired 1,2-di(anthracen-9-yl)ethyne or 1,2-bis(9-anthryl)acetylene, BisAA (5),^{21–23} in 68% in the last reaction step. All physical properties and spectroscopic data agree with the values reported in the literature. More details about the synthetic procedures and characterization for each step are included in the Supporting Information.

Steady-state absorption spectra were acquired in a Cary 50 spectrometer, and fluorescence spectra were acquired in a Cary-Eclipse fluorimeter (Varian). Our fluorescence upconversion setup has been described in detail elsewhere.^{24–26} For excitation we used the second harmonic pulses from a regeneratively amplified Ti:sapphire laser with a 1 kHz repetition rate. The polarization of the pump-pulse was adjusted to magic angle conditions with respect to the detection axis (vertical) with a 400 nm half-wave plate, and then focused to the sample with a 30 cm focal length lens. The solutions were studied in a rapid flow quartz cell (2 mL/s) of 1 mm optical path length. The fluorescence from the sample was collected with a pair of parabolic mirrors and focused in a 0.5 mm β -BBO upconversion crystal where it was gated with pulses separated from the fundamental beam (800 nm) and time delayed. The polarization of the gate pulses was adjusted to the vertical direction (crystal's ordinary axis) with a half-wave plate. The resulting sum-frequency mixing signal was collected with a 5 cm diameter lens and focused into a double monochromator to be detected with a photomultiplier tube. The detector signal was passed through an oscilloscope and connected to a lock-in amplifier (Stanford Research Systems). The signal was

modulated to 1/3 of the laser repetition rate by a phase locked optical chopper (New Focus). The upconversion instrumental response function is mainly limited by the optical path length in the cell and was determined from upconversion of the solvent Raman signals to be Gaussian with a full width at half-maximum of 490 fs. In all cases, back-to-back scans with the solvent only were acquired to ensure that the signals are not contaminated by the upconversion of scattered light or other artifacts.

Computational Method. The ground state geometry of BisAA was optimized at the B3LYP/6-311+G(d,p) level of theory. The effects of the solvent were taken into account through the polarizable continuum model IEFPCM. The energies of different conformations with a varying dihedral angle between the anthracenic moieties were calculated in the electronic ground state. For this, the twist angle was set constant at different values and the rest of the degrees of freedom were optimized. The Gaussian 09 set of programs was used for all calculations.²⁷ It should be noticed that we only include calculations for the ground state in order to understand some details of its potential energy surface. From previous studies in BA, the respective calculations of the excited states of these symmetric model compounds in solution will require the use of highly specialized methods which include explicit solvent molecules and account for their polarizability.²⁸

RESULTS AND DISCUSSION

Figures 1 and 2 show the absorption and emission spectra of BisAA in cyclohexane and acetonitrile. As can be seen, the

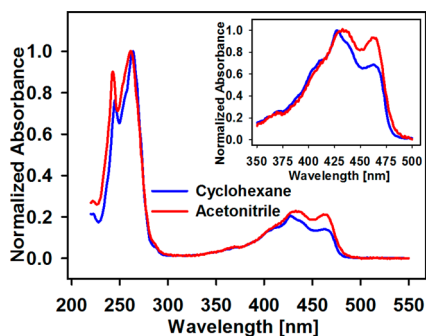


Figure 1. Absorption spectra of BisAA in cyclohexane and acetonitrile solutions. The inset shows details of the first absorption band.

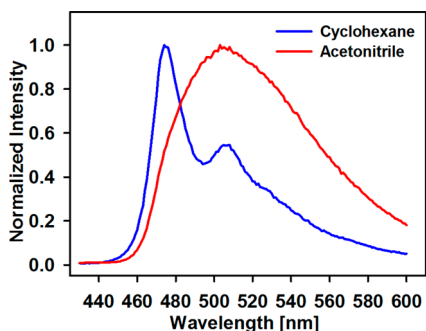


Figure 2. Emission of BisAA in cyclohexane and acetonitrile solutions. The excitation wavelength was 400 nm.

absorption spectra are not significantly altered in going from a nonpolar to a polar solvent. This is expected from a symmetric non-dipolar electronic ground state. The absorption spectrum of BisAA is similar to that of anthracene with the presence of a

low energy band at 441 nm and an intense band at 266 nm. Such similarity with the anthracene absorption spectrum is consistent with an anthracene-localized transition, similar to the case of BA.²⁸ The red shifting of the first absorption of BisAA in comparison with anthracene (356 nm) can be explained as an effect of a substitution on the short molecular axis of this chromophore which is the direction of the respective transition dipole moment. A localized transition is expected if the BisAA molecule does not retain a fully planar structure as observed in the crystal phase.^{21,29} Theoretical calculations at the density functional level of theory (see Figure 3) indicate that, in fact, in

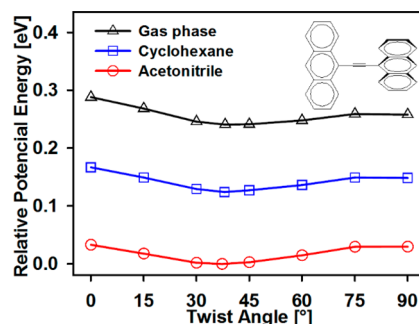


Figure 3. Potential energy of electronic ground state for BisAA as function of the twist angle between the anthryl groups in the gas phase, in cyclohexane and acetonitrile solutions. The level of theory was B3LYP/(IEFPCM)/6-311+G(d,p).

the ground state, BisAA does not correspond to a fully planar conformation in gas and solution phases, but that, instead, an angle between the two anthryl units of about 38° exists (38.2° in the gas phase, 38.0° in cyclohexane, 37.3° in acetonitrile). Small energy barriers for BisAA at this level of theory are observed for torsional angles of 0° and near 90°. These barriers are approximately 0.4 and 1.2 kcal/mol respectively in the gas phase. As has been explained previously,¹⁵ such small barriers imply a preferential conformation in acetylene-bridged systems (at near 38° BisAA), although they are small enough to produce a distribution of conformations.

Differently from the absorption spectra, for the emission spectra, clear red shifting and shape changes take place when going from cyclohexane to acetonitrile solutions. Particularly, the fluorescence spectrum in cyclohexane maintains clear anthracenic type vibronic structure, while the acetonitrile solutions show a broad emission which is Stokes shifted by 1822 cm⁻¹, corresponding to a CT state type emission. This emission is very similar to the one for BA in polar solvents.^{5,6} We have performed studies of the emission in cyclohexane and acetonitrile as a function of concentration to verify the absence of effects like ground state association or the formation of excimers. The results are included in the Supporting Information where the concentration of BisAA was varied by more than 7 orders of magnitude below the working concentration of the upconversion measurements. The emission spectra do not show any changes as a function of concentration, which is indicative of the absence of intermolecular processes like the formation of aggregates or excimers.

Figures 4 to 6 show the emission spectrum of BisAA in a series of solvents. In solvents of low polarity like dichloromethane (DCM) and tetrahydrofuran (THF), the emission spectra of BisAA appear to be formed by a superposition of the

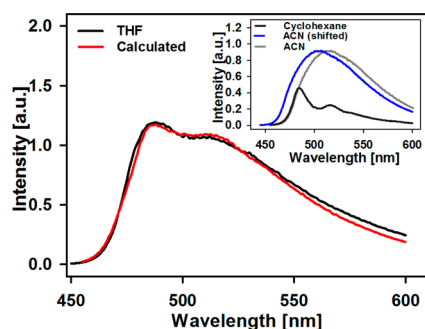


Figure 4. Emission spectra of BisAA in tetrahydrofuran (black) and calculated (red) from contributions in cyclohexane (0.22) and acetonitrile (0.78). Inset: weighted area normalized emission spectra of BisAA in cyclohexane, acetonitrile (ACN), and acetonitrile left shifted by 10 nm (ACN shifted).

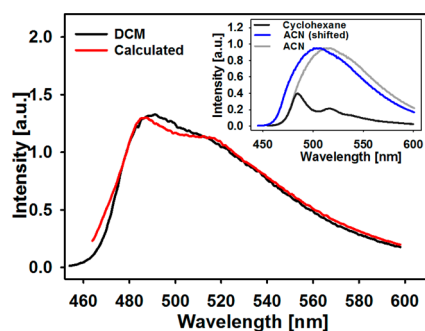


Figure 5. Emission spectra of BisAA in dichloromethane (DCM, black) and calculated (red) from contributions in cyclohexane (0.19) and acetonitrile (0.81). Inset: weighted area normalized emission spectra of BisAA in cyclohexane, acetonitrile (ACN), and acetonitrile left shifted by 10 nm (ACN shifted).

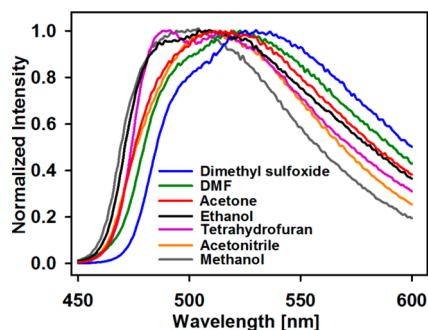


Figure 6. Steady-state emission spectra for BisAA solutions in several polar solvents. DMF: *N,N*-dimethylformamide.

cyclohexane and acetonitrile type emissions. In fact, as shown in Figures 4 and 5, the fluorescence from the THF and DCM solutions can be approximated by a weighted sum of the emission in cyclohexane, plus the emission in acetonitrile after a 10 nm shift to shorter wavelengths. The necessity of shifting the acetonitrile component to produce a good match between the constructed spectrum (cyclohexane emission + shifted acetonitrile emission) with the THF and DCM spectra is due to the dependence of the CT type emission on the solvent polarity (see below). The observation that, in these low polarity solvents, both LE and unstructured red-shifted type emissions are observed is indicative of an equilibrium between two types of states.

Further, we have employed the method of Kowski and co-workers to estimate the dipole moments of the ground and CT excited state of BisAA in polar solvents.^{30–35} For this, we measured the spectral position of the first absorption and the CT state type emission in a series of polar solvents (Figure 6). The emission data ($\bar{\nu}_{\text{abs}} - \bar{\nu}_{\text{fluor}}$) and ($\bar{\nu}_{\text{abs}} + \bar{\nu}_{\text{fluor}}$) was plotted as a function of the polarity parameters $f(\epsilon, n)$ (eq 1) and the sum $f(\epsilon, n) + 2g(n)$ (eq 2) as shown in Figure 7,

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

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

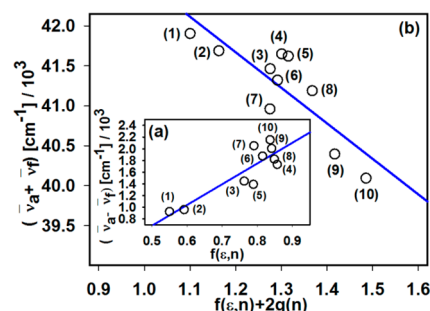


Figure 7. Plots of (a) Stokes shift ($\bar{\nu}_a - \bar{\nu}_f$) and (b) sum of absorption and emission maxima ($\bar{\nu}_a + \bar{\nu}_f$) as a function of the solvent polarity parameters $f(\epsilon, n)$ and $f(\epsilon, n) + 2g(n)$ respectively. Solvents in (a) and (b): (1) tetrahydrofuran, (2) dichloromethane, (3) isopropanol, (4) methanol, (5) propanol, (6) ethanol, (7) acetone, (8) acetonitrile, (9) *N,N*-dimethylformamide, and (10) dimethyl sulfoxide.

where n is the refractive index and ϵ the dielectric constant of each solvent. The method of Kowski et al.³⁵ takes the slopes from the linear fits of both plots: m_1 from Figure 7(a) and m_2 from Figure 7b to estimate the dipolar moment in the ground and CT emissive states using eqs 3 and 4 respectively:

$$\mu_{\text{ground}} = \frac{m_2 - m_1}{2} \sqrt{\frac{hca^3}{2m_1}} \quad (3)$$

$$\mu_{\text{excited}} = \mu_{\text{ground}} \frac{(m_2 + m_1)}{m_2 - m_1} \quad (4)$$

where a is the radius of the respective Onsager cavity radius (here taken as 5.95 Å). The result of this analysis estimates a S_0 dipole moment of 1.1 ± 0.90 D and of 9.7 ± 2.9 D for the CT state (the uncertainties were propagated from the uncertainties in the slopes in the linear regression analysis). The approximately 9.7 D dipole moment for the CT state in BisAA is similar to that determined for BA of approximately 8 D.^{5,36} This analysis of the Stokes shifting of the CT band confirms the highly dipolar nature of the emissive state in polar solvents in this molecule.

Turning to the time-resolved studies, the femtosecond fluorescence upconversion results for BisAA in cyclohexane and acetonitrile solutions are shown in Figures 8 to 11. The spectral evolutions of the emission bands were constructed from the single wavelength upconversion scans together with the corresponding normalization procedure which uses the steady-state spectra and multiexponential fits to the single

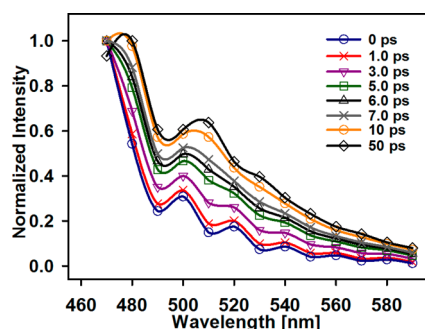


Figure 8. Normalized spectral evolution resolved at several delay times for BisAA in cyclohexane solution.

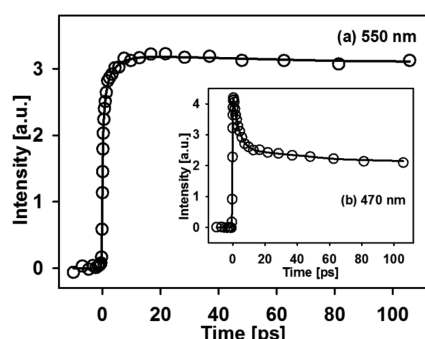


Figure 9. Femtosecond resolved fluorescence intensity for BisAA in cyclohexane solution at (a) 550 nm and (b) 470 nm; the excitation wavelength was 400 nm. Solid lines correspond to fits to multiexponential functions convoluted with the instrumental response function.

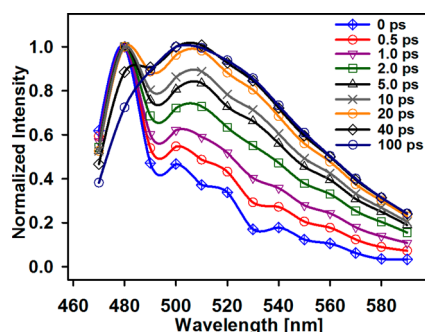


Figure 10. Normalized spectral evolution resolved at several delay times for BisAA in acetonitrile solution.

wavelength traces.³⁷ As can be seen (Figure 8 (cyclohexane), Figure 10 (acetonitrile)), the evolution of the transient emission spectra in both solvents corresponds to a reshaping of the bands with increases in the relative signal intensity on the red side of the spectra and with decreases in the blue region. While spectral reshaping is observed in both solvents, the changes as a function of time are much more pronounced in the acetonitrile solutions than in the cyclohexane samples where the changes are minimal.

As can be seen in Figure 8, for the cyclohexane sample at times near $t = 0$, the spectrum appears somewhat more structured than at later times with a large peak at 470 nm. As time elapses, the spectrum acquires some extra amplitude in the region above 500 nm, however, the largest intensity at all times corresponds to the highest energy peak. This peak shifts only slightly to approximately 480 nm after a few picoseconds. Since

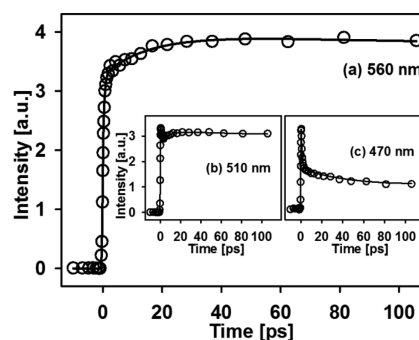


Figure 11. Femtosecond resolved fluorescence intensity for BisAA in acetonitrile at (a) 560 nm, (b) 510 nm, and (c) 470 nm. The excitation wavelength was 400 nm. Solid lines correspond to fits to multiexponential functions convoluted with the instrumental response function.

the steady-state fluorescence spectrum in cyclohexane is considered to be dominated by emission from a LE state, these changes are related mainly to vibrational relaxation and not to the formation of a full CT state. Two of the single wavelength traces of BisAA in cyclohexane are included in Figure 9. For 470 nm, the $t = 0$ peak, we observe a fast decay of 3.1 ps followed by a second decay of 21 ps, and finally, a long-lived signal which corresponds to the emissive state lifetime. Since the time range of our upconversion experiments does not allow for a full decay of this signal, we estimated the lifetime to be $\tau_{\text{lifetime}} > 1.0$ ns. Inspection of the spectral evolution in cyclohexane indicates that the rapid 3.1 ps decay at 470 nm is due to the slight shifting of the high energy peak to approximately 480 nm. The 21 ps component is related to smaller amplitude changes in the spectrum and is considered to be due to vibrational relaxation which produces changes in the width of the vibronic emission peaks. As will be elaborated in more detail below (see evolution of the first spectral moment), the 21 ps component at 470 nm does not result in further changes of the average energy of the transition.

The single wavelength trace at 550 nm for BisAA in cyclohexane is characterized by an initial rise behavior with a time constant of 1.1 ps and the same lifetime component. The early signal rise at this wavelength is considered to be due to the same relaxation process which produces the 3.1 ps decay at 470 nm. Importantly, at 550 nm no further accumulation of intensity is observed (that is, a near 21 ps component is absent, see description of the first spectral moment given below).

Given the fast accumulation of emission signals in the 490–520 nm region of the spectrum, and with similar considerations as in the studies of BA, it can be suggested that, even in the non-dipolar cyclohexane, a small population of what has been called a *partial charge transfer state* (PCT)^{4,12–14} may exist in equilibrium with the nonpolar LE state. The stabilization of a PCT state in the non-dipolar solvent cyclohexane has been explained already for BA to be due to interactions with induced dipole moments in the solvent.^{4,12} Most importantly, however, it is clear that the spectral evolution for BisAA in cyclohexane does not result in the appearance of a full CT emission (acetonitrile type) at any time scale, and that the fluorescence in this solvent is largely dominated by the LE state.

As mentioned, the spectral evolution in acetonitrile (Figure 10) shows much larger changes. In this solvent, starting at $t = 0$, a cyclohexane-like emission (mainly LE emission) evolves into the broad, Stokes shifted steady-state emission. Differently from

the case of the less dipolar solvents, this spectral evolution produces a final spectrum (see $t = 100$ ps, Figure 10) which does not appear to be a composite as in the case of THF and DCM (Figures 4 and 5). From this consideration, already evident in the steady-state spectra, it can be concluded that, in acetonitrile, the full population of excited states evolves into the full CT state represented by the broad Stokes shifted band. Importantly, the spectral evolution for BisAA in acetonitrile occurs on two well differentiated time scales as described in terms of the first spectral moment (see below).

Importantly, in acetonitrile, the spectrum at $t = 0$ is clearly similar to that observed in the nonpolar solvent, with a clear intense vibronic peak at 480 nm, which shows that the excitation event initially produces the nonpolar LE state in acetonitrile. As can be seen in Figure 11, the single wavelength trace at 470 nm, which is near the $t = 0$ LE emission peak, shows an initial fast decaying term of 0.8 ps which is followed by an intermediate decay of 36.9 ps and a $\tau_{\text{lifetime}} \geq 3.0$ ns component (lifetime component, see below).

The single wavelength trace at 510 nm, in the central spectral region for the BisAA/acetonitrile sample, shows a fast decay of 0.95 ps, but is followed by a rise of 9.8 ps, which is then followed by the lifetime decay of $\tau_{\text{lifetime}} \geq 3$ ns. On the red side of this spectrum, the traces show two rising components. For example, at 560 nm, the first rising component is 0.67 ps and the second one is 11.6 ps (560 nm), which is then followed by the ≥ 3 ns lifetime decay. The rising components seen in the region near the CT state emission maxima and on its red side are a signature of the accumulation of emission from the CT state.

A more quantitative description of the evolution of the transient spectra in both solvents can be obtained from the time evolution of the first spectral moment:

$$M_1 = \frac{\int I(t, \nu) \nu \, d\nu}{\int I(t, \nu) \, d\nu} \quad (5)$$

which is shown in Figure 12 for cyclohexane and Figure 13 for acetonitrile. While in cyclohexane this evolution occurs as a

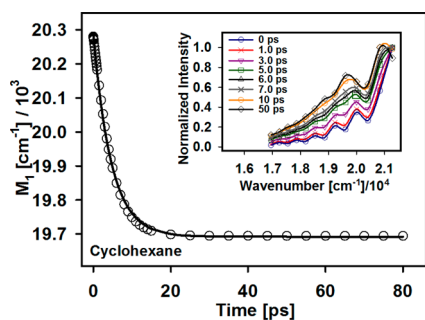


Figure 12. First spectral moment (M_1) as function of time for BisAA in cyclohexane. Solid lines correspond single-exponential plus a constant fits. Inset: Normalized spectral evolution resolved at several delay times for BisAA in cyclohexane solution as a function of wavenumber.

single exponential change of the M_1 values, with a time constant of 4.64 ps; in acetonitrile, the M_1 evolution is clearly biphasic, with a first exponential of $\tau_1 = 0.92$ ps, and a much slower one of $\tau_2 = 37.3$ ps.

As mentioned previously, the spectral changes represented by the single exponential M_1 function for the BisAA/

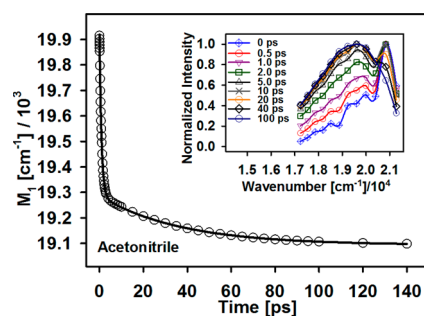


Figure 13. First spectral moment (M_1) as function of time for BisAA in acetonitrile. Solid lines correspond to biexponential plus a constant. Inset: Normalized spectral evolution resolved at several delay times for BisAA in acetonitrile solution as a function of wavenumber.

cyclohexane sample are related to the vibrational relaxation of the system which might include a small contribution from an equilibration between the LE state and a PCT state in analogy with what has been observed for BA.^{6,12,14} On the other hand, in acetonitrile, the fast term in the biphasic behavior has to do with the onset of an equilibrium between the LE state and a PCT state (see below), but is followed by a second stage which involves a much slower time scale associated with the equilibration into the fully relaxed CT state.

The assignment of the onset of the LE \rightleftharpoons PCT equilibrium during the fast part of the M_1 evolution in acetonitrile is well supported by inspection of the $t = 1$ ps spectrum in this solvent: This spectrum is included in Figure 14 (black circles), where

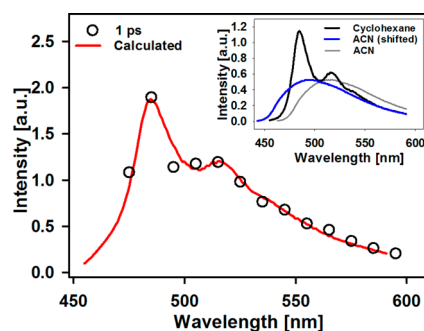


Figure 14. Time-resolved emission spectrum of BisAA in acetonitrile at $t = 1$ ps (black circles) and calculated (red line) from contributions in cyclohexane (0.55) and acetonitrile (0.45). Inset: weighted area normalized emission spectra of BisAA in cyclohexane, acetonitrile (ACN), and acetonitrile left shifted by 20 nm (ACN shifted) used to form the calculated spectrum.

we also show a spectrum calculated as the superposition of the steady-state cyclohexane spectrum (LE) and the steady-state acetonitrile spectrum shifted by 20 nm to the blue (red line). The similarity of the $t = 1$ ps in acetonitrile with the composite spectrum shows that the system has relaxed in the time scale of the first M_1 component into an equilibrium between the LE state and a PCT type state represented by the shifted acetonitrile spectrum (gray line in the inset of Figure 14).

It should be noted that the spectral shifting accounted by the first decay of M_1 of 0.92 ps approximately matches the diffusive solvation time of acetonitrile (0.089 ps (inertial), 0.63 ps (diffusive)),³⁷ indicating that this part of the evolution is most likely be dictated by the solvent response. This is further suggested by the previous experimental and theoretical studies on BA, a compound which should have a polarizability

comparable with that of BisAA. More specifically: In the computational study of BA by Grozema et al.,²⁸ which used a mixed molecular mechanics/quantum mechanics simulation scheme, it was shown that the dipolar moment in the BA solute is induced by solvent reorganization in a subpicosecond time scale. This is consistent with the dynamics observed experimentally for BA,^{5,7,8,12–14} and with the fast component in the spectral evolution observed herein for BisAA of 0.92 ps. The solvent is considered to be the main driver in this process since the asymmetry in the electron distribution of the solute can be achieved in an extremely fast time scale through small amplitude fluctuations of the solvent configuration.²⁸ It should be noted also that the study by Grozema et al. showed that, in moderately polar solvents, the dipolar state formed after excitation corresponds to an inter-anthryl orientation slightly different from BA's perpendicular conformation of the ground state. In the case of BisAA, it is also possible that the interchromophore dihedral angle undergoes a small change during the subpicosecond component, although from the time scale and previous results, we estimate that spectral response is primarily solvent-induced in this time scale.

Most importantly for the BisAA system, the second part of the spectral evolution takes place in a much longer time scale, an order of magnitude slower than the solvation times in acetonitrile. Also, this component is completely absent for BA in acetonitrile solution. Accordingly, the long component for the red-shifting in acetonitrile of 37.3 ps should be associated with changes in the molecular conformation, which allows a larger degree of charge separation.²⁸

Although potential energy curves for BisAA excited states are not currently available, it is likely that, along the torsional coordinate, there may exist small energy barriers of the order of 1 kcal/mol (similar to the ground state case, see Figure 3), and which are likely to define the 37.3 ps time scale. A relevant reference point in this regard is rate constant for the photoisomerization of *trans*-stilbene. This chromophore is of comparable dimensions to BisAA and is similar to the present case in the sense that electronic excitation gives a large degree of rotational freedom around the central bond. The *trans*-stilbene isomerization involves an activation energy of 3.5 kcal/mol, and it has been observed that these rates in solution are 10-fold faster than in the gas phase.³⁸ This effect is due to the solvent participation in intramolecular vibrational redistribution (IVR) and direct reaction activation along the relevant coordinate.³⁹ The time scales for *trans*-stilbene isomerization in solution are several tens of picoseconds depending on the solvent.³⁸

From our review of the literature, it is clear that, at present, the time scales for isomerization or conformational changes around triple bonds in excited states are not described thoroughly. However, a relevant example does exist.¹⁵ In studies of butadiyne-linked porphyrin dimers, it was observed that, upon electronic excitation to the first singlet state, where barriers for rotation are of the order of 2 kcal/mol, the conformations of these systems undergo perpendicular to planar changes with a rate constant of the order of 10^{10} s^{-1} .⁴⁰ For the BisAA system, the ground state has a barriers of around 1 kcal/mol for the dihedral coordinate. These small barriers in BisAA appear to reflect an interplay between the extension of the molecular conjugation and a very small degree of steric hindrance between the anthracenic peri-hydrogens (see Figure 3). If in the excited state of BisAA the barriers are of a similar magnitude, time scales of tens of picoseconds for geometry

equilibration are reasonably expected and consistent with the 37.3 ps time constant. It should be noted that, for the evolution in acetonitrile, such conformational change is necessarily coupled to the dipole moment increment of the solute (charge transfer), given that we observe a further 200 cm^{-1} red-shifting in this time scale. In the definition of this time scale, it is considered that the solvent still plays a dominant role as in the case of *trans*-stilbene,³⁹ through induced IVR and directed reaction activation. From analogy with the BA system, the final geometry of the CT state may also approach a near 90° disposition of the anthryl units.

The kinetic scheme associated with the formation of the CT state in BisAA/acetonitrile accommodates perfectly the models put forward by Jurczok et al.,⁶ Takaya et al.,¹² and Asami et al.,⁴ where an initial equilibrium between the LE and a partial charge transfer state PCT takes place before the system is able to relax to the full CT state:¹²



This scheme, developed in detail by Takaya et al., predicts the biexponential decay we observe in the region of the LE state and the multiexponential accumulation of signal in the spectral region dominated by the CT state. The theoretical prediction of the actual geometry of the first electronically excited state in BisAA (CT in polar solvents) will require sophisticated models for the solvent effects. Specifically, it has been concluded previously that dielectric continuum methods are not sufficient to describe the symmetry breaking observed in BA. Instead, methods where the solvent and its polarizability are treated explicitly will be needed for such kind of studies.²⁸ It should be noticed that we have focused on the study of BisAA in acetonitrile solutions since this solvent does not have solvation components in the picosecond time scale, as is the case of all alcohols and practically all other polar solvents. Therefore, acetonitrile is an excellent model solvent (and nearly the only one) which is polar enough to form a full CT state, and in which the solvent response times do not interfere with the time scales in the picosecond range in which part of the dynamics are observed.

CONCLUSIONS

We have studied the formation of a charge transfer state of BisAA after electronic excitation in solution. Similarly to the classic model compound BA, BisAA shows a Stokes shifted emission spectrum in acetonitrile and other polar solvents, indicative of a charge transfer state. The femtosecond resolved emission from this molecule in acetonitrile shows that the fluorescence resembles that of a LE state at times near zero after excitation, and that it evolves to the broad Stokes shifted band of the CT state in two different time scales. The first fast part of the evolution is similar to the time scale for the diffusive response of the solvent. Most importantly, the second component of 37.3 ps is much slower than the solvent response times and is indicative of the relaxation of the excited state structure which allows for further stabilization of the CT state. This intramolecular coordinate most likely corresponds to a change in the relative orientation of the two anthracenic end groups of the molecule.

Our results show that BisAA is a new and interesting model to describe charge separation in solution and particularly of the symmetry reduction associated with going from a highly polarizable LE state to the CT state, with well separated time scales for the evolution along the solvent and intramolecular

coordinates. The bridging acetylenic group that joins the two anthracenes plays the role of giving enough separation between the end groups to reduce the steric interactions and, also, to maintain electronic coupling between them. The present model compound is an extension from the classic BA model which suffers from a restriction in the available conformational space due to steric hindrance between the two anthracenes. The BisAA system is presented as a new system to test and extend models for the electron transfer dynamics which involve an intramolecular coordinate.

■ ASSOCIATED CONTENT

■ Supporting Information

Detailed synthetic procedures, BisAA steady-state emission spectrum at different concentrations in cyclohexane and acetonitrile and full ref 27. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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