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An *N*,*N*′-diaryl urea based conjugated polymer model system

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Abstract—An *N*,*N*′-diphenyl urea was designed as a model system for aggregation phenomenon in poly(phenyleneethynylenes) (PPEs). The unmethylated *N*,*N*′-diphenyl urea adopts an open, unfolded conformation in which the two diphenyl acetylene fluorophores are far enough away, mimicking the unaggregated state. Dimethylation forces the aromatic surfaces together into π–π contact, mimicking the aggregated state of PPEs. Analogous to bulk PPEs, this model system shows dramatic differences in quantum yield between the folded and unfolded states, with the unfolded urea having greater than 400-fold higher fluorescence quantum yield than its folded equivalent.

Polymer morphology and supramolecular ordering can have a dramatic effect on optical properties and thus, can either improve or diminish the utility of a polymer for a particular application.[1] For example, poly(phenyleneethynylenes) (PPEs) have a quantum yield in solution approaching unity. On the other hand, solid state devices based on thin films of PPEs have dramatically lower quantum yields.[2] These differences presumably arise from the differences in the properties between the aggregated and unaggregated PPEs. A better understanding of the emission properties of polymer aggregates could, therefore, lead to improvements in PPE based devices. However, the study of the aggregated state of conjugated polymers is difficult because the observed emission behavior of the bulk material arises from a combination of different aggregated and unaggregated structures. One solution has been to design model systems that fold the conjugated polymer onto itself, quantitatively mimicking intramolecular interactions of the aggregated state. Typically, two conjugated polymer chains are attached to a rigid U-shaped template, which forces the two chains into a parallel π–π stacked conformation (Fig. 1a). Examples of appropriate U-shaped templates including: 1,8-anthracene, 1,8-naphthalene, *para*-phenylcyclophanes, *meso*-porphyrins, ethane, and *ortho*-benzene.[3]

We report, herein, a new PPE model system based on an *N*,*N*′-diphenyl urea template that can serve as both a model of the aggregated and unaggregated states. Comparison of the respective emission properties of the *cis*,*cis* and *trans*,*trans* conformers (Fig. 1b) can then be used to help gauge the effects of aggregation behavior on the emission properties of PPEs. Control of the diphenyl urea conformation was effectively exerted by alkylation. Unmethylated *N*,*N*′-diphenyl urea exists in the *trans*, *trans* conformations in which the phenyl groups are in a divergent ‘unfolded’ conformation.[4,5b] Dimethylation reverses the conformational preferences as the sterically larger methyl groups occupy the *trans*-position adjacent to the carbonyl oxygen. This forces the two phenyl rings together into the folded *cis*,*cis* conformation. Azumaya and co-workers have demonstrated that folded *cis*,*cis* ureas are effective U-shaped templates for the study of π-stacking interactions.[5c] Bradley Smith has utilized the ability to control the *cis*,*cis* to *trans*,*trans* equilibrium as a supramolecular switch. Lewis et al. has also used the

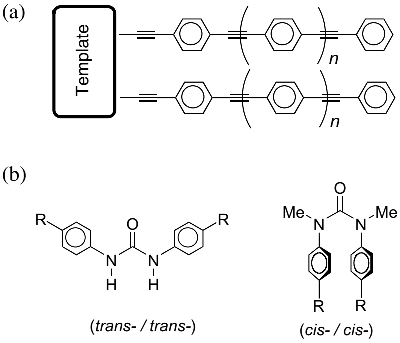

Figure 1. Representation of a model system for conjugated polymer aggregation based on a rigid U-shaped template.

Keywords: Urea; Conjugated polymers; Fluorescence.

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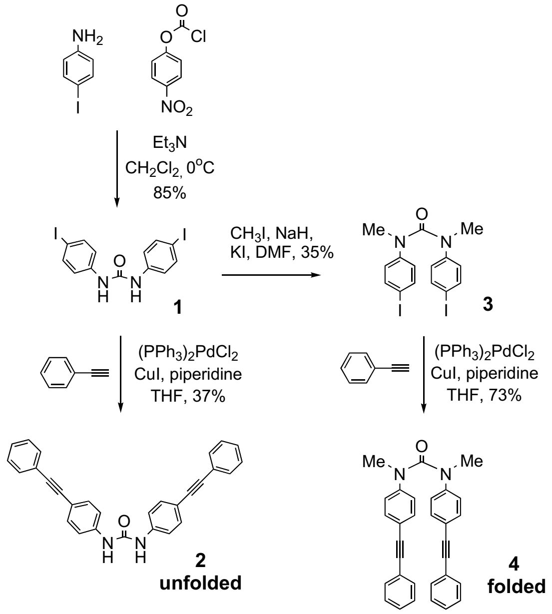
folded shape of N,N'-dimethylureas to study molecular structure and luminescence.[5a] These studies have demonstrated that in the folded *cis*,*cis* conformer, the two phenyl rings are in π–π contact and the π-systems can effectively communicate, while in the unfolded *trans*,*trans* conformer the two phenyl rings are far apart.[5]

Another attractive characteristic of the chosen model system was that it is easily assembled from common precursors (Scheme 1). N,N'-Diiododiphenyl urea **1** was prepared by treatment of *p*-nitrophenyl chloroformate with an excess of *p*-iodoaniline in triethylamine and dry dichloromethane. This urea was coupled to phenyl acetylene via a Sonogashira[6] coupling to give the unfolded urea **2**.

Conversion of **1** to the N,N'-dimethyl derivative **3**, is obtained by alkylation with methyl iodide, sodium hydride, and potassium iodide in anhydrous DMF. Compound **3** was then coupled to phenyl acetylene under Pd/Cu catalyzed conditions to give folded urea **4**.

The expected folded *cis*,*cis* and unfolded *trans*,*trans* conformations of **4** and **2** were verified by ^{1}H NMR and X-ray spectroscopy. Comparison of the ^{1}H NMR from both the methylated (**4**) and unmethylated **(2)** showed dramatic differences consistent with the expected folded and unfolded conformations (Fig. 2). The aryl protons *ortho* to the urea are shifted approximately 0.5 ppm upfield for the methylated urea **4**, which is characteristic of π–π stacking and formation of the folded *cis*,*cis* conformation.[5b] The same protons in urea **2** are further downfield, which is consistent with an unstacked *trans*,*trans* conformation.

The respective conformations were further established from X-ray crystal structures and molecular modeling (Fig. 3). Crystals of dimethylated urea **4** were grown from tetrahydrofuran. The crystal structure of **4** is in the folded *cis*,*cis* conformation. However, the arms are not completely parallel and are skewed due to the short N–N distance (2.34 Å) of the urea template and the 53.9° N_{urea}–C_{aryl} tortional angle between the two arms. The first aromatic rings of the diphenyl acetylene arms are within π–π stacking distances; whereas, the terminal phenyl rings are far apart (9.1 Å). An interesting thing to note is that only three C_{aryl} atoms of the first phenyl ring are within the necessary distance for π–π stacking (<3.6 Å).



Scheme 1. Synthesis of folded and unfolded ureas **4** and **2**.

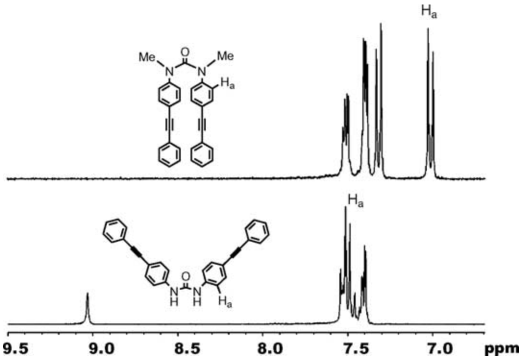


Figure 2. ^{1}H NMR spectra of the folded **4** and unfolded **2** in DMSO-d_6.

Crystals of the unfolded unmethylated urea **2** could not be solved. However, many examples of N,N'-diphenyl ureas exist in the literature and they all are in the *trans*,*trans* conformation.[4] Molecular modeling of urea **2** is consistent with the literature and predicts that it will be in the unfolded *trans*,*trans* conformation in which the two diphenyl acetylene arms are in a divergent conformation and cannot interact by π–π stacking.

Once the folded and unfolded structures of **4** and **2** were established, their spectroscopic properties were examined in acetonitrile (Table 1). The UV–vis spectra were consistent with previous studies on methylated and

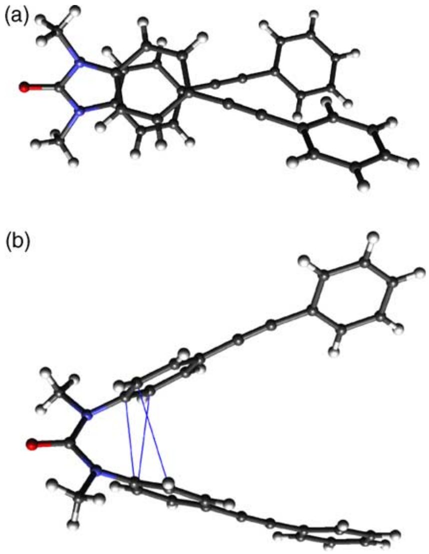


Figure 3. Top (a) and side (b) views of X-ray crystal structure of folded urea **4**. Close contacts (<3.6 Å) between the two diphenyl acetylene arms are shown as blue lines.

unmethylated diphenyl ureas. The $\lambda_{\max}$ of folded dimethylated urea **4** were typically blue shifted in comparison with unfolded urea **2**. This blue shift of the aggregated model system is consistent with the folded poly(*m*-phenyleneethynylene)s (*m*PPEs) studied by Moore.[7] However, aggregation studies on poly(*p*-phenylene-ethynylene)s (*p*PPEs) show the reverse trend with the formation of a sharp aggregation band at higher wavelength. It is perhaps not surprising that the urea model system is more consistent with the *m*PPEs as they share similar diphenyl acetylene chromophores.

Differences in the fluorescence spectra between **2** and **4** were even more pronounced (Fig. 4). Unfolded urea **2** had an intense fluorescence with emission maxima at 348 nm. Folded urea **4**, in contrast, showed significantly lower fluorescence with a broad peak centered at 454 nm. The dramatically lower fluorescence of the aggregated model system is again consistent with that observed by Moore in *m*PPEs. The *m*PPEs in their unfolded state have a strong fluorescence maximum at 340 nm. Whereas, folded *m*PPEs have a very weak red shifted fluorescence at 425 nm.[7] Similar trends are also seen in *p*PPEs, where the unaggregated state displays a strong fluorescence at 430 nm and the aggregated state displays a weak fluorescent band at 500 nm.

The fluorescence efficiencies were quantified by measurement of the respective quantum yields in solution (Table 1). Unfolded and folded ureas **2** and **4** had quantum yields of 0.85 and 0.002, respectively. The differences are similar in trend but not in magnitude to what is observed for the unaggregated ($\Phi_f = 1.0$) and aggregated ($\Phi_f = 0.13$) *p*PPEs.[1c] The 425-fold difference in fluorescence efficiencies of **2** and **4** are again more similar to the *m*PPE foldamers.[7]

Table 1. Spectroscopic maxima and quantum yields (Φ_f) of ureas, all measured at room temperature in acetonitrile

Urea	UV–vis $\lambda_{\max}$/nm	Fluorescence	
		λ_f/nm	Φ_f
2	323	348	0.85
4	294	454	0.002
7	305	378	0.11

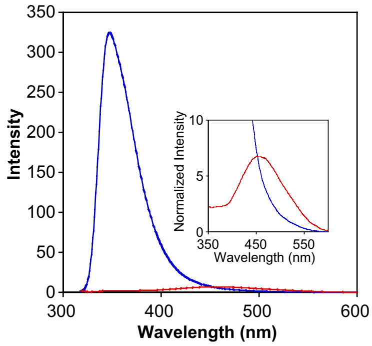


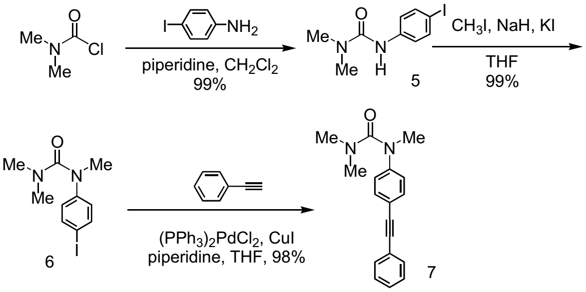
Figure 4. Fluorescence of ureas **2** (blue) and **4** (red) at 2.5×10^{-6} M at 23 °C in acetonitrile.

To confirm that the differences in fluorescence of **2** and **4** arose solely from their different conformations, two control experiments were conducted to rule out the possibility of intermolecular aggregation and the presence of small amounts of quenching impurities. First, the absorbance spectra of both **2** and **4** showed a linear dependence of absorbance with respect to concentration in the concentration range of the spectroscopic experiments. This suggests that there is no intermolecular aggregation in the concentration range of the fluorescence measurements. Secondly, to rule out the possibility of small amounts of quenching impurity in **4** resulting in the much lower observed fluorescence, the fluorescence of a solution containing a mixture of **2** and **4** was measured and found to be similar to the sum of the two independent fluorescent spectra. This suggests that there are no significant quenching impurities in **4** as their presence would have also lead to a much lower observed fluorescence for the mixture.

The difference in fluorescence between **2** and **4** could arise from a combination of two sources. The first is from quenching due to interaction of the two chromophores in the folded conformation. The second possible source is due to the loss of conjugation of the urea nitrogen with the diphenyl acetylene chromophore upon methylation. In the crystal structure of folded urea **4**, the urea nitrogen is twisted out of plane with the aryl ring. The C_{urea}–N_{urea}–C_{aryl}–C_{aryl} torsional angle averages 40.5°. To investigate the contribution of each of these sources, a 'one-arm' model system **7** was synthesized in which the urea nitrogen is twisted out of plane with the aromatic ring but does not have a second arm thus eliminating the contribution of the chromophore–chromophore interaction.[8]

First, urea **5** was synthesized by reacting *p*-iodoaniline with dimethyl carbamyl chloride and piperidine in dry dichloromethane to give **5** quantitatively (Scheme 2). Methylation of **5** with iodomethane, sodium hydride, and potassium iodide in dry THF yielded **6**. Pd/Cu coupling of **6** to phenyl acetylene yielded the one-arm urea **7**.

The absorbance and fluorescence spectra of the one-armed urea **7** fall directly between those measured for folded and unfolded ureas **4** and **2** (Table 1). For example, the fluorescence maximum of 378 nm is between the values of 454 and 348 nm for **4** and **2**. This suggests that both the loss in conjugation of the urea



Scheme 2. Synthesis of one-armed urea **7**.

with the diphenyl acetylene chromophores and the thru-space interactions of the two chromophores contribute to the lower fluorescence efficiencies of folded urea **4**. Based on the comparisons of their quantum yields, the primary contributor to the lower fluorescence of **4** was due to the thru-space interactions of the chromophores as the differences in quantum yield between **7**and **4** were approximately 50-fold. The smaller contributions of the disruption in the conjugation of the urea nitrogen and the diphenyl urea chromophore is seen by the smaller 7-fold difference in quantum yield between **7** and **2**.

In conclusion, models based on a *N*,*N*′-diaryl urea template were studied to better understand the difference in emission properties of PPEs in the aggregated and unaggregated states. Analogous to behavior seen for PPEs, a dramatically higher emission intensity was observed for the unfolded urea that mimics the unaggregated state in comparison to the folded urea that mimics the aggregated state. Specifically, unfolded urea **2**, exhibits a greater than 400-fold increase in fluorescence efficiency over the folded urea **4**. The conjugation length is shorter in the folded urea due to the twisting of the C_{aryl}–N_{urea} bond and it is feasible that thru-space interactions between the folded arms of **4** could be the major contributing factor as to the decrease of fluorescence. Even though there is minimal contact between the two arms, via only three aryl-carbons, this contact is just enough to drastically decrease fluorescence efficiency and red shift the fluorescent spectra.

Acknowledgements

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