

Molecular Wire Behavior in π -Stacked Donor-Bridge-Acceptor Tertiary Arylureas

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We report here the dynamics of photoinduced charge separation and charge recombination in a series of donor-bridge-acceptor (D-B-A) oligo(arylureas) possessing a pyrene (Py) hole donor and dimethylaniline (DMA) hole acceptor as capping groups separated by zero-to-four phenyl bridging units (**1–5**, Figure 1a). These ureas adopt folded face-to-face geometries with slightly splayed π -stacked phenyl rings, similar to that reported by Yamaguchi et al. for a urea having phenyl capping groups and three bridging units.¹ The efficiency and dynamics of charge separation and charge recombination have been determined by means of femtosecond (fs) broadband pump–probe spectroscopy. Formation of a charge-separated state is rapid and highly efficient, independent of the length of the bridge. Rate constants for charge separation and charge recombination in ureas **3–5** are weakly dependent upon the number of bridging phenyls, thus providing the first example of wire-like behavior in a synthetic π -stacked D-B-A system.

Ureas **1–5** and the reference molecules **6** and **7** (Figure 1b) were prepared by methods analogous to those we have employed previously for the synthesis of capped oligo(arylureas).^{2,3} The optimized gas-phase structure for urea **3** obtained from semi-empirical AM1 computational analysis (Figure 1c) and the upfield shift of protons on the phenylenediamine bridge in the ¹H NMR spectra support the conformational preference of these “protophanes” for folded geometries.⁴ The UV spectra of **2–6** display a weak band at 375 nm and a stronger structured band at 350 nm,⁴ similar to those of other pyrene derivatives.³ The spectrum of **1** has a single broad long-wavelength band. ZINDO calculations support the assignment of the long wavelength bands of **2–6** to Py-localized transitions and the band of **1** to a DMA-to-Py charge-transfer transition.⁵

Transient absorption spectra for ureas **1–6** in acetonitrile solution were determined with a spectral range of 300–700 nm and resolution of 5–7 nm using 347 nm excitation from a Ti-sapphire-based system having a time resolution of ca. 100 fs at time intervals between 0 and 1900 ps.³ Transient spectra for ureas **1**, **5**, and **6** are shown in Figure 2. Transient spectra for **2–4** resemble those for **5**.⁴ In the case of **1**, a narrow band at 500 nm assigned to Py^{•+} is formed with a rise time of 0.5 ps (Figure 2a). Also formed at short times are a broad band around 600 nm and a band with two resolved maxima centered at 380 nm. Both of these bands are assigned to DMA^{•+} based on their similarity to the absorption spectrum obtained by means of spectroelectrochemistry of urea **7** (Figure 2a). The decay of the 380 and 600 nm bands of **1** is best fit by a dual exponential function.

In the cases of **2–6**, a broad band around 500 nm and a narrower band with a single maximum at 380 nm, both of which are assigned to Py S₁ (Figure 2b,c), are formed within several picoseconds via internal conversion from S₂.³ The appearance of the transient spectra of **2–5** then change to resemble that of **1**. The rise time of the

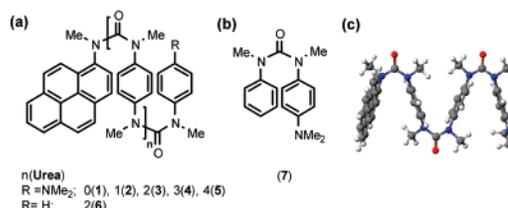


Figure 1. Structures of ureas **1–7** and AM1 optimized geometry of **3**.

narrow Py^{•+} 500 nm band increases from 8.1 ps for **2** to 20.7 ps for **5**. The 600 and 380 nm bands attributed to DMA^{•+} grow in on the same time scale. Following these changes, the 380, 500, and 600 nm bands of **2–5** decay with similar single exponential decay constants. In the case of **6**, hole injection into the bridge can occur but is not accompanied by the change in the 380 nm band shape observed for **2–5**. Charge recombination of **6** is best fit as a dual exponential having a minor long-lived component that is not observed for **1–5**.

The rise and decay times for ureas **1–6** are summarized in Table 1. The ultrafast exergonic charge separation and charge recombination for **1** is analogous to that for other donor–acceptor dyad systems.^{3,6} The behavior of ureas **2–5**, as illustrated for **5** in Figure 3, is different from that of **1**. The single exponential rise of the 500 nm Py^{•+} band and the concomitant formation of the 600 nm band and the double maximum 380 nm band assigned to DMA^{•+} is attributed to bridge-mediated hole transport rather than single-step superexchange, on the basis of its weak distance dependence. The similar 500 nm rise times for **3–5** and the control molecule **6** suggests that hole injection from Py S₁ into the adjacent bridging phenyl is at least partially rate determining and that hole transport to DMA in **3–5** occurs on the same time scale as hole injection. The slower 500 nm rise for **2–6** versus **1** is consistent with the higher oxidation potentials of the bridging phenyls⁷ versus the reference urea **7**.⁸ The simultaneous decay of the 380, 500, and 600 nm bands of **2–5** is assigned to bridge-mediated charge recombination in which charge delocalization into the bridge (de-trapping) is at least partially rate determining. Since charge recombination is slower than hole transport, the efficiency of charge separation is high for all bridge lengths.

Plots of the log of the rate constants for charge separation ($k_{cs} = \tau_r^{-1}$) and charge recombination ($k_{cr} = \tau_d^{-1}$) versus center-to-center Py–DMA distance for **1–5** are shown in Figure 4. Linear fits of the data for **3–5** provide values of the attenuation factors $\beta = 0.005 \text{ \AA}^{-1}$ for charge separation and 0.01 \AA^{-1} for charge recombination. The values of β are similar to those reported for D-B-A systems having oligo(*p*-phenylenevinylene) linkers that display molecular wire behavior.⁹ Faster k_{cs} and k_{cr} for **2** may reflect the occurrence of tunneling at short distances. We attribute the wire-like behavior of the oligo(phenylurea) bridges to hole delocalization. ZINDO calculations show extensive delocalization of holes on two adjacent bridging phenyls, in accord with the measured oxidation potentials of the oligo(phenylureas)⁷ but hole localization on the

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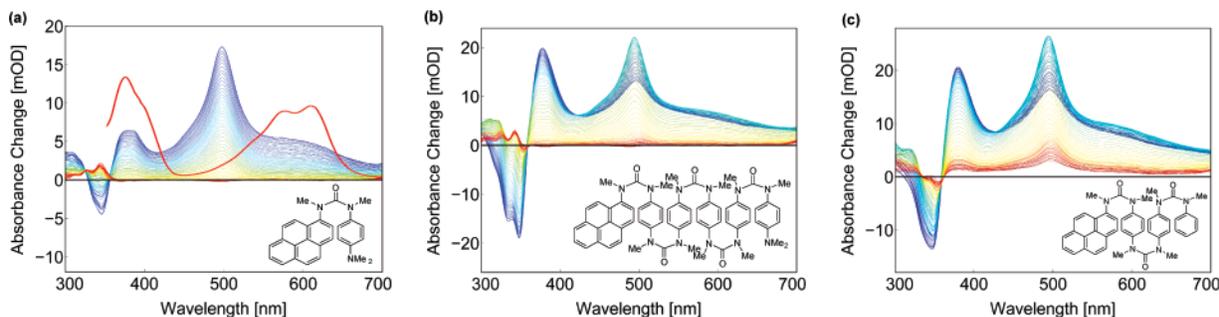


Figure 2. Temporal evolution of the pump–probe spectra of ureas (a) **1**, (b) **5**, and (c) **6** in the time range of 5–1900 ps following 347 nm excitation in acetonitrile. Early spectra are shown in blue/green colors and late spectra in orange/red colors. The absorption spectrum of **7**⁺ acquired by spectroelectrochemistry is shown as the red overlay in (a).

Table 1. Femtosecond Pump–Probe Transient Data for Ureas **1–6**^a

urea	τ , ps (380 nm)	τ , ps (500 nm)
1	12 (0.003); 85.4 (0.005)	0.5 (r); 12 (0.008); 90 (0.01)
2	57	8.1 (r); 61
3	91	19 (r); 103
4	101	20 (r); 119
5	107	21 (r); 126
6	79 (0.03); 1260 (0.004)	24 (r); 100 (0.03); 1620 (0.008)

^a All components are decaying components, unless otherwise noted. Amplitudes are in parentheses; r = rising components.

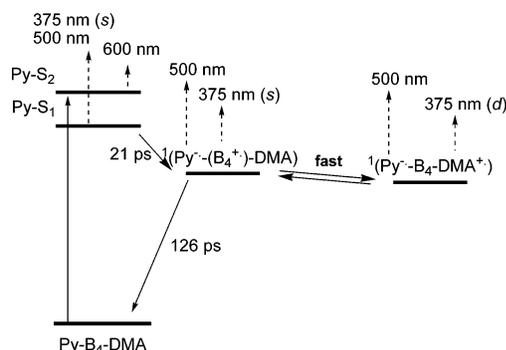


Figure 3. Excited-state behavior of urea **5** (broken arrows indicate transient assignments; s = single peak; d = double peaks).

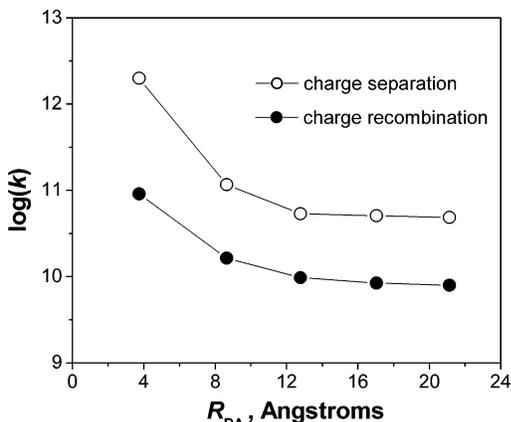


Figure 4. Distance-dependent kinetics for charge separation and charge recombination of ureas **1–5**.

capping DMA.⁴ Thus the hole can move rapidly through the oligo-(phenylurea) bridges in either the forward (charge separation) or return (charge recombination) direction.

Vinyl polymers possessing pendant aromatic groups capable of π -stacking are known to display high hole mobilities both in solution and in the solid amorphous state.¹⁰ Rate constants as high as $6 \times 10^9 \text{ s}^{-1}$ (180 ps) have been reported for aryl–aryl hole

transport in poly(*N*-vinylcarbazole) derivatives; however, lower hole mobilities are found for smaller aromatic pendant groups such as naphthyl or phenyl. High hole mobility is associated with delocalization over two or more π -stacked aromatic groups. Modification of the ends of oligomers with donor and acceptor groups has been suggested as a means of probing the distance dependence of hole transport in self-stacking systems.¹¹ This has been accomplished for porphyrin-bridge-quinone systems assembled with zero-to-two 1,8-diarylnaphthyl linkers ($\beta = 0.43 \text{ \AA}^{-1}$)¹² and for duplex oligonucleotides modified with synthetic donor and acceptor groups separated by base pair domains of varying length and base sequence.¹³ Hole transport in long DNA A-tracts displays weak distance dependence with estimated rates of 50 ps to 1 ns per base pair, slower than in D-B-A systems having oligo(*p*-phenylene-vinylene) bridges. The present results establish that wire-like behavior can be achieved by means of electronic coupling in a π -stacked bridge.

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Supporting Information Available: Experimental details, including synthesis and characterization, NMR and absorption spectra, AM1 optimized structures, absorption spectra and transient spectra for ureas **1–6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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