

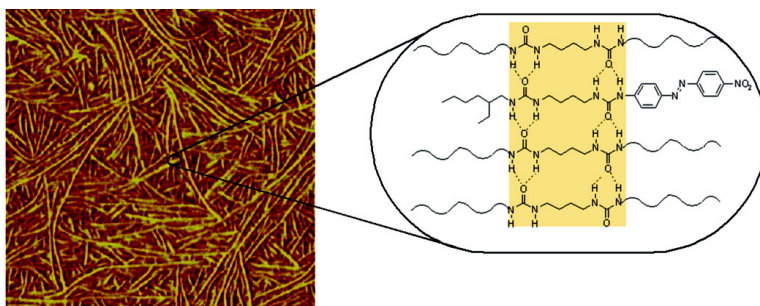
Article

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Molecular Recognition in a Thermoplastic Elastomer

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Abstract: Selective incorporation of bisurea guests in thermoplastic elastomers with poly(tetrahydrofuran) soft blocks and bisurea containing hard blocks is observed when the distances between the urea groups of host and guest match. The incorporation leads to significant modulation of mechanical properties. With bisurea-functionalized dyes as guests, a strong difference in extractability by detergent solution was shown between dyes differing by just one methylene unit between urea groups. Upon elongation of elastomer films, strong differences in alignability of matching and nonmatching dyes were observed.

Introduction

Molecular recognition in polymers is used extensively to selectively bind small molecules or ions, and it provides a powerful tool for the modulation of materials properties.^{1–4} In elastomeric polymers, reversible alignment of, for example, covalently attached azobenzenes molecules⁵ or noncovalently embedded fluorescent dyes⁶ by mechanical deformation of the polymeric matrix has been used to tune the optical properties of the resulting materials. Smith et al. studied the orientation of dyes and π -conjugated polymers that were blended with polyolefins.⁷ Subsequently drawing the films resulted in highly oriented chromophores, with dichroic ratios exceeding 20.

Here, we demonstrate the design of thermoplastic elastomeric hosts bearing uniform bisurea recognition units⁸ and size-selective guests that self-assemble into supramolecular ribbons (Figure 2) to form functional materials.

Urea groups are known to associate strongly via bifurcated hydrogen bonds,⁹ whose strength exceeds that of amide and urethane hydrogen bonds. Several research groups have utilized

the strong association between low molecular weight compounds containing bisurea groups to obtain gelling agents.¹⁰ Thermoplastic elastomers (TPEs) containing urea groups have also been synthesized before.¹¹ There are, however, only a few examples of TPEs possessing hard blocks comprising solely urea groups.¹² Block copoly(ether)ureas **1** and **2** (Chart 1) are a new class of thermoplastic elastomers containing urea groups. They consist of poly(tetrahydrofuran) (pTHF) soft segments ($M_n = 1100$) and

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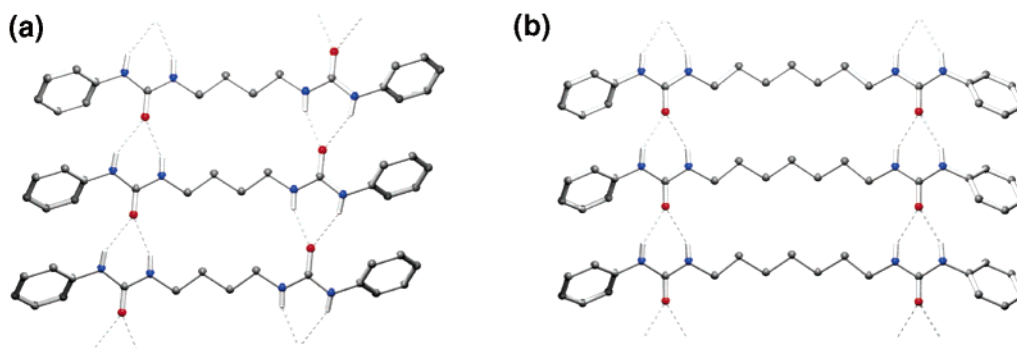


Figure 1. Single-crystal X-ray structure of **3** (a) and **4** (b).

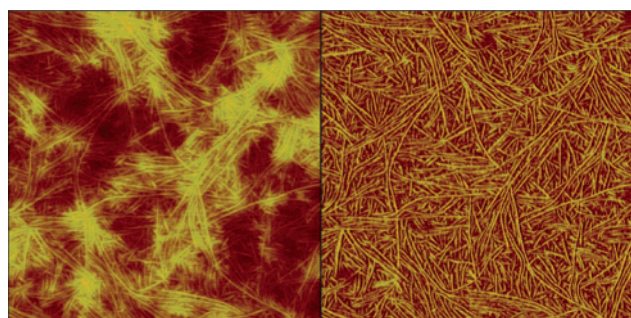


Figure 2. AFM images ($1 \mu\text{m}^2$) of thermoplastic elastomer **1**; height (left) and phase contrast (right).

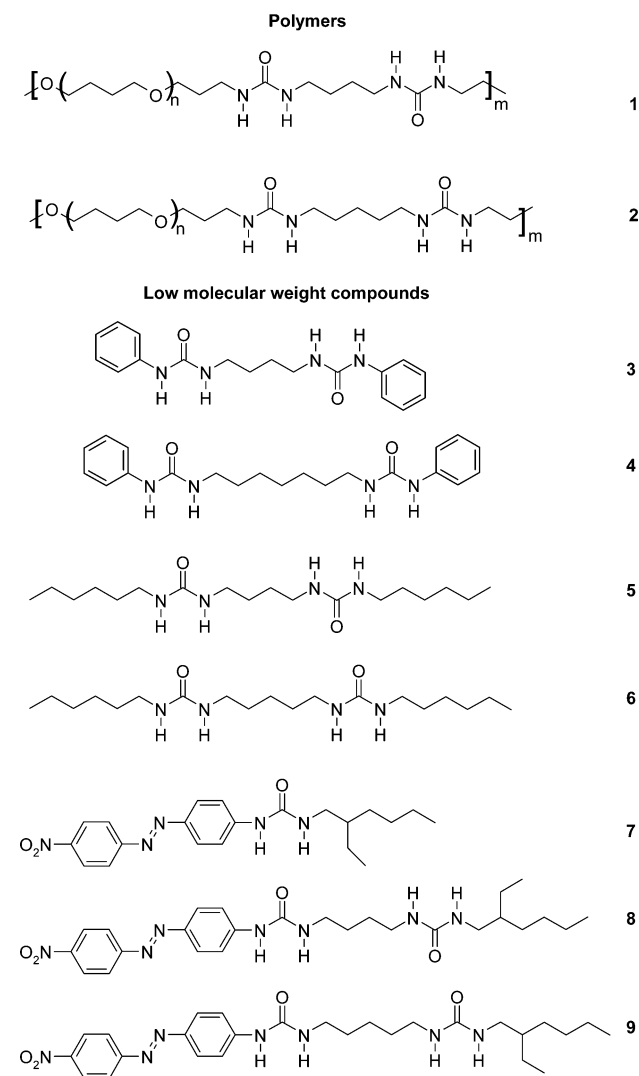
uniform bisureido-butylene or bisureido-pentamethylene hard segments for **1** and **2**, respectively. Association of the hard segment domains via hydrogen bonding results in the formation of reversible cross-links embedded in a soft, rubbery, amorphous pTHF matrix. The design of thermoplastic elastomers with uniform bisurea hard blocks allows for the incorporation of guest molecules bearing a bisurea moiety via a “perfect-fit” principle. In this way, modification of the polymer properties, or functionalization of the material, can be effectuated in a modular approach by simply mixing the complementary guests (Chart 1) with the polymers. Furthermore, we show that the optomechanical properties of the host–guest material are modulated in a selective manner.

Results and Discussion

Design of Selective Host–Guest System. To gain more insight into the way bisurea units associate via hydrogen bonding, crystals were grown from two model compounds (Figure 1) containing an “even” bisureido-butylene (**3**) and an “odd” bisureido-heptylene unit (**4**). After synthesis, single crystals suitable for X-ray analysis were obtained by slow diffusion of water vapor into a 50 g/L solution of **3** or **4** in DMSO.

The all-trans conformation of the “even” butylene spacer leads to a transoid arrangement of the two urea groups, whereas the all-cis conformation of the “odd” heptylene spacer leads to a cisoid arrangement of the two urea groups. The urea groups and the spacer are virtually coplanar. The angles between the least-squares planes through the urea group and through the carbon atoms or the spacer are $7.84(10)^\circ$ for structure **3** and $2.78(7)^\circ$ for structure **4**. Bifurcated hydrogen bonding between adjacent urea groups gives rise to the formation of an infinite stack of hydrogen bonds, with a spacing between the two hydrogen-bonded urea groups of $4.64(8) \text{ \AA}$ for the “even” butylene spacer and $4.63(10) \text{ \AA}$ for the “odd” heptylene spacer.

Chart 1. Compounds **1–7**



This is comparable to the distance in crystal structures of substituted urea groups described in the literature.^{8b,9,10b,e,f}

To see whether block copoly(ether)ureas **1** and **2** with a uniform bisurea hard block would form similar long stacks via hydrogen bonding of the urea groups as described above, the morphology of **1** was studied with AFM in the tapping mode.¹³ Figure 2 shows the resulting AFM images, in which the hard phase appears lighter than the soft phase.

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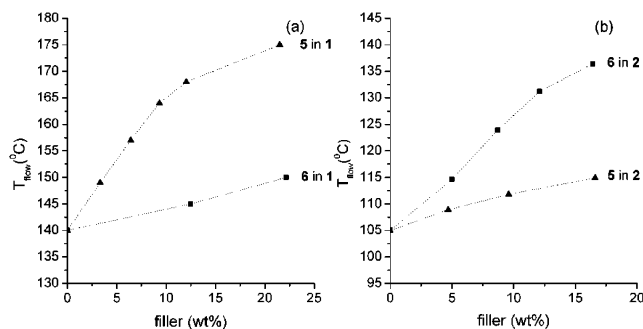


Figure 3. Flow temperature of **1** (a) and **2** (b) as a function of the amount of reinforcement filler **5** or **6**. Lines are used as a guide for the eyes.

The AFM images show long fibers with a length of up to 500 nm and an apparent width of 10 nm. Smaller details cannot be discerned since the dimensions of the AFM tip limit the resolution. The fibers most probably consist of stacks of bisurea hard blocks embedded in the soft matrix. The stacks were used to intercalate guest molecules functionalized with a bisurea recognition unit.

Modification of Polymer Properties. Polymers **1** and **2**, differing from each other by just one methylene group between urea groups, are rubberlike materials with flow points of 140 and 105 °C, respectively. The molecular weights M_n (as determined with GPC) of **1** and **2** are 45×10^3 and 50×10^3 g/mol, respectively. They have an elastic modulus of 95.8 and 93.0 MPa, respectively, plastic deformation sets in at $\lambda = 100\%$, and the elongation at break is approximately 1060%.^{13,14} The relative orientations of the urea groups in the hard blocks of these TPEs are expected to be transoid and cisoid based on the odd–even effect (four and five methylene units, respectively) observed in the crystal structures of model compounds **3** and **4** (four and seven methylene units). The effects of **5** and **6** as additives¹⁵ (four and five methylene units between urea groups) on the thermomechanical properties of **1** and **2** are remarkably different. Solution cast films of **1** containing **5**, a low molecular weight bisurea compound matching the hard block of **1**, were transparent up to 12 wt %. In contrast to this, films of **1** containing **6**, which has a nonmatching pentamethylene spacer between its two urea groups, were turbid because of phase separation even when small amounts (1 wt %) of the additive were added. The effect of the presence of different amounts of **5** or **6** on the flow temperature of **1** and **2**, as determined with

optical microscopy, is shown in Figure 3. An increase of the flow temperature of **1** from 140 to 175 °C was observed upon addition of 20 wt % of filler **5**, whereas the flow temperature only increased to 150 °C upon addition of the same amount of **6**, strongly suggesting preferred incorporation of **5** in the hard blocks of **1**.

A similar trend is observed for mixtures of **2** and nonmatching and matching additives **5** and **6**, supporting the preferred incorporation. The flow temperature of **2** increased from 105 to 137 °C upon addition of 17 wt % of **6**, whereas it only increased to 113 °C upon addition of the same amount of **5**.

Selective Extraction of Dyes. To further study molecular recognition within block copoly(ether urea)s, 0.25 wt % of bisurea-functionalized azobenzene dyes **8** or **9**, having four and five methylenes in the spacer between the urea groups, were incorporated in films of thermoplastic elastomers **1** and **2**. Combining these compounds gave two matching polymer–guest pairs (**1** + **8** and **2** + **9**) and two nonmatching pairs (**1** + **9** and **2** + **8**). In none of the films was phase separation observed with optical microscopy. Four similar-sized pieces were cut from these films, and they were individually stirred in 0.1 M sodium dodecyl sulfate solutions at 60 °C. Extraction of the dyes was followed with UV–vis spectroscopy of the solutions. The results depicted in Figure 4 show that the dyes containing bisurea units that match the hard block of the elastomer are extracted more slowly and to a lesser extent than the nonmatching dyes. After 60 h, only 38% of the complementary dyes was extracted from the film compared to approximately 80% of noncomplementary dyes, demonstrating the size selectivity of the dye incorporation. The consistently higher extractability of nonmatching dyes excludes differences in solubility between the dyes as a possible cause for the effect.

Differential dye extraction was also studied in thin fibers of **1** and **2** produced by electrospinning, a technique that produces fibers of nanometer to micrometer size in diameter. A polymer solution is slowly pumped through a millimeter size nozzle that is connected to a high-voltage supply (12 kV). Under the applied electrostatic force, the polymer is ejected from the nozzle as a fiber whose diameter is reduced significantly as it is transported and deposited on a grounded template.¹⁶ In this way, materials with a high surface-to-volume ratio can be obtained, with interesting applications ranging from nanofiber-reinforced composite materials¹⁷ to supports for enzymes¹⁸ and catalyst¹⁹ to sensors.²⁰

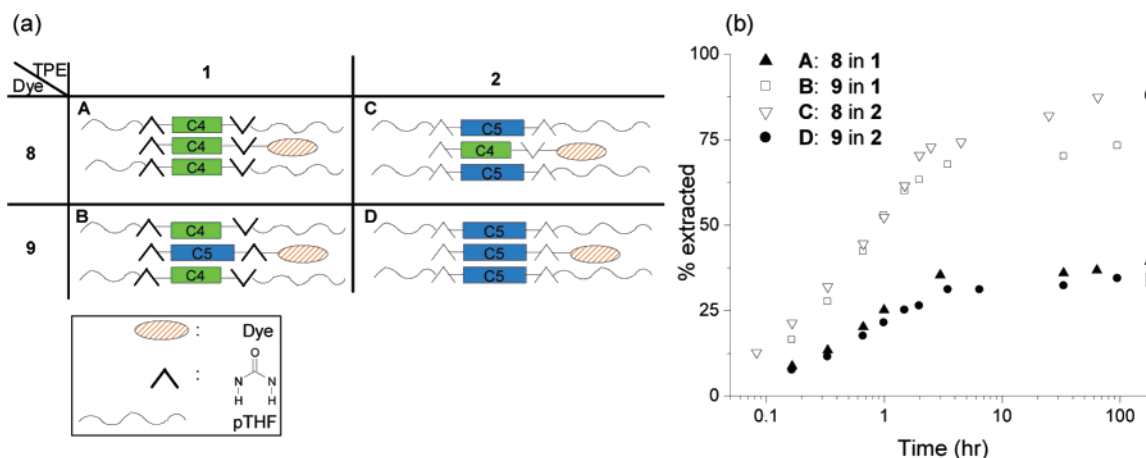


Figure 4. (a) Table showing combinations of TPEs and dyes used in extraction experiments. (b) Percentage of dyes **8** and **9** extracted from films of **1** and **2** by aqueous SDS solution as determined with UV–vis spectroscopy.

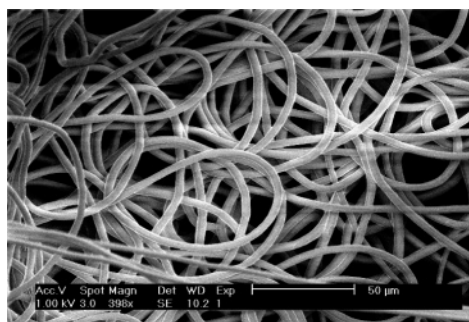


Figure 5. SEM image of electrospun sample of **2** containing 0.25 wt % of **9**.

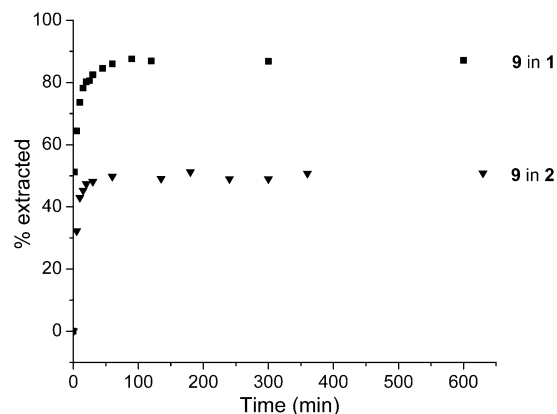


Figure 6. Percentage of **9** extracted from dyed electrospun fibers of **1** and **2** as determined with UV-vis spectroscopy.

Fibers containing 0.25 wt % dye **9** were spun and analyzed with SEM, showing very uniform fibers with a diameter of approximately 5 μm (Figure 5).

Extraction of the dyes, as described above for films of **1** and **2**, was repeated with dye **9** incorporated in electrospun fibers of noncomplementary polymer **1** and complementary polymer **2**. The extraction kinetics were much faster in the electrospun fibers because of the increased surface area-to-volume ratio, and furthermore, slightly more of the dye could be extracted: whereas extraction of films took several hours, extraction reached its final value of 90 and 50%, respectively, after 20 min for the electrospun fibers (Figure 6).

Dye Orientation. Orientation and alignment of dyes by mechanical deformation is a useful way to modulate optical properties of polymer films.^{6,7} The present system offers interesting possibilities to perform mechanical alignment in a guest-selective manner. To study guest-selective orientation, we first investigated mechanical orientation of urea blocks of host polymers **1** and **2** with infrared linear dichroism spectroscopy,¹³

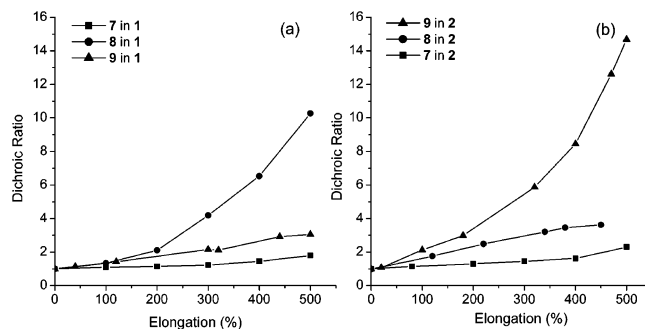


Figure 7. Dichroic ratio as a function of the elongation of dyed films of **1** (a) and **2** (b).

a technique that has often been used to study the orientation of functional groups within polymers.²¹ This technique has shown strain-induced orientation of hard segments in polyether urethane ureas to be perpendicular to the deformation axis at strains beyond the yield point.²² In films of **1**, the dichroic ratio of absorption bands due to stretch vibrations was measured with polarized infrared light parallel and perpendicular to the deformation axis. Significant differences were observed between dichroic ratios of bands arising from the hard segment at $\nu = 3325 \text{ cm}^{-1}$ (N-H stretching vibration) and 1615 cm^{-1} (C=O stretching vibration) and from the soft segment at $\nu = 1110 \text{ cm}^{-1}$ (C-O-C stretching vibration). The dichroic ratio of the urea groups in the hard segments reaches values of close to 5 at high strains, indicating that the chain axis of the hard segment orients parallel to the deformation axis, while the dichroic ratio of the soft pTHF blocks remains below 1.5.

Orientation of dye chromophores was studied by UV spectroscopy in films of **1** and **2** containing small amounts (0.25 wt %) of dye molecules **7**, **8**, or **9** prepared by dissolving both components in a chloroform/methanol mixture and casting the solution in a Petri dish. UV-vis spectra were measured at 0° and 90° polarization angles with respect to the deformation axis, and the dichroic ratio was determined at λ_{max} .

Upon elongating films of **1** containing 0.25 wt % of complementary **8**, the dichroic ratio increased rapidly, reaching values of 11 for $\lambda = 500\%$ (Figure 7a), indicating that the chromophore of the dye is oriented parallel to the deformation axis upon stretching the film. On the other hand, the dichroic ratio for noncomplementary dye **9** does not exceed a value of approximately 3, while for monourea-functionalized dye **7** the dichroic ratio remains below 2, indicating that both **7** and **9** do not orient as strongly as **8**. Similar trends were observed for films of **2** to which were added 0.25 wt % of matching dye **9** or nonmatching dyes **7** and **8** (Figure 7b). After relaxation of samples of **1**, which were strained to 500%, residual strain was 220%, indicating significant plastic deformation. The dichroic ratio of **8** decreased from 11 to 4.7 after releasing the stress, while for **9** as guest the dichroic ratio decreased from 3 to 1.5.

The high dichroic ratio observed in elongated films of matching dye and TPE indicates specific incorporation of urea-functionalized dyes in the hard domain of the elastomer resulting in

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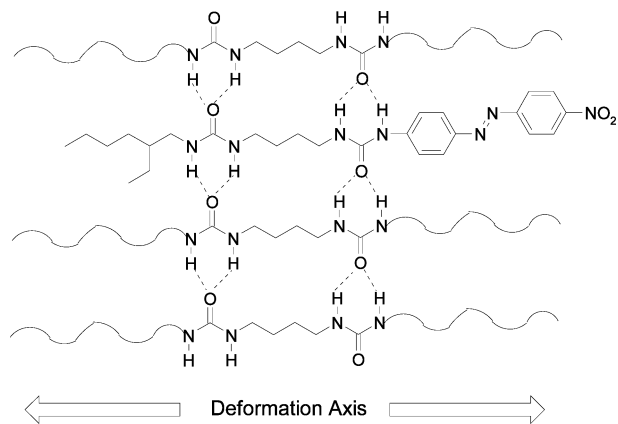
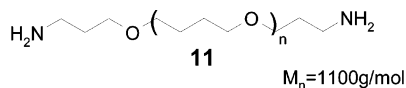


Figure 8. Schematic representation of dye **8** in the hard block of an elongated film of **1**.

orientation of the transition dipole moment of the dye parallel to the deformation axis. This is schematically depicted in Figure 8.

The much lower dichroic ratio of nonmatching dyes is in line with the predominant location in the more weakly oriented amorphous phase.

Further support for the different locations of matching and nonmatching dyes comes from the positions of λ_{\max} for matching pairs of dye and elastomer ($\lambda_{\max} = 406$ nm) and nonmatching pairs of dye and elastomer ($\lambda_{\max} = 420$ nm). The latter λ_{\max} is close to the value of 423 nm found for both dyes in amine-terminated pTHF prepolymer **11**, the molecule constituting the soft phase of the TPEs. However, the fact that the shape of the absorption band does not change upon going from a matching to a nonmatching host is a good indication that the dye molecules are not self-aggregated in either of these host phases.



For the matching pairs of dye and elastomer, the perpendicularly polarized λ_{\max} shifted from 406 to 414 nm upon

elongating the films above 300%, whereas no shift was observed for the nonmatching pairs. Absorption of light with this polarization is mainly caused by nonoriented dye molecules. This is a strong indication that also the matching dyes are partly present in the pTHF soft block. Thus, both dye extraction and dye orientation experiments allow the conclusion that matching dyes are taken up preferentially in the hard blocks, while nonmatching dyes are predominantly present in the soft block.

Conclusions

We have shown that length-dependent molecular recognition between bisurea units in an elastomeric host results in selective modulation of mechanical properties. Strong discrimination between guests differing in size by a single methylene group was observed. Incorporation of bisurea containing dye molecules in the hard blocks of the polymer is also selective, resulting in different extractabilities of the dyes by detergent solutions. The guest selectivity of the elastomeric material can be used to selectively orient dyes upon elongation of thin films. With the possibility to draw functionalized fibers by electrospinning, we introduce a modular approach for thermoplastic meshes with a variety of applications. Work along this line is in progress.

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Supporting Information Available: Synthesis and characterization of compounds **3–9**, experimental procedures, displacement ellipsoid plots for compounds **3** and **4** (PDF), and details of the structure determinations of compounds **3** and **4**, including atomic coordinates and displacement parameters (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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