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Sterically Controlled Recognition of Macromolecular Sequence Information by Molecular Tweezers

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Abstract: Sequence-specific binding is demonstrated between pyrene-based tweezer molecules and soluble, high molar mass copolyimides. The binding involves complementary $\pi-\pi$ stacking interactions, polymer chain-folding, and hydrogen bonding and is extremely sensitive to the steric environment around the pyromellitimide binding-site. A detailed picture of the intermolecular interactions involved has been obtained through single-crystal X-ray studies of tweezer complexes with model diimides. Ring-current magnetic shielding of polyimide protons by the pyrene "arms" of the tweezer molecule induces large complexation shifts of the corresponding ^{1}H NMR resonances, enabling specific triplet sequences to be identified by their complexation shifts. Extended comonomer sequences (triplets of triplets in which the monomer residues differ only by the presence or absence of a methyl group) can be "read" by a mechanism which involves multiple binding of tweezer molecules to adjacent diimide residues within the copolymer chain. The adjacent-binding model for sequence recognition has been validated by two conceptually different sets of tweezer binding experiments. One approach compares sequence-recognition events for copolyimides having either restricted or unrestricted triple−triplet sequences, and the other makes use of copolymers containing both strongly binding and completely nonbinding diimide residues. In all cases the nature and relative proportions of triple−triplet sequences predicted by the adjacent-binding model are fully consistent with the observed ^{1}H NMR data.

Introduction

Noncovalent recognition of sequence information in linear macromolecules underpins the whole of biology, most notably perhaps in protein synthesis where aminoacyl-*t*-RNAs undergo templated polycondensation on the ribosome via sequential recognition of triplet monomer sequences in *m*-RNA[1] and in the operation of restriction enzymes which catalyze the cleavage of DNA with complete sequence specificity.[2] However, despite tremendous advances in synthetic supramolecular chemistry over the past 20 years, the recognition of sequence information in high molar mass copolymers by small molecules of complementary structure has remained an almost entirely biological phenomenon.[3] Initial results have recently been described on "self-sorting" in synthetic polymer systems, in which small-molecule receptors bind at complementary positions on a polymer chain,[4] and in preliminary communications we have reported that different pyromellitimide-centered sequences in aromatic copolyimides such as **1** can be recognized selectively by the electron-rich "tweezer molecules" **2** and **3** (Chart 1).[5,6] In such systems the different tweezer-imide binding constants give rise to markedly different ^{1}H NMR complexation shifts $\Delta\delta$ of the corresponding pyromelitimide resonances. This type of sequence recognition depends on complementary $\pi-\pi$ complexation between pyromellitimide units and the electron-rich pyrenyl tweezer arms. Related interactions have also recently been used to direct supramolecular assembly in diimide systems,[7] to promote chain-folding in aliphatic polyetherimides,[8] and to generate double-stranded, "zipper"-type supramolecular complexes.[9] Many different types of π-donor tweezer molecules and their complexes with π-acceptor aromatics, have been described in the literature,[10] but investigations of their supramo-

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Chart 1. Copolyimide (**1**) Containing Different Pyromellitimide-Centered Sequences, and Tweezer Molecules **2** and **3**.

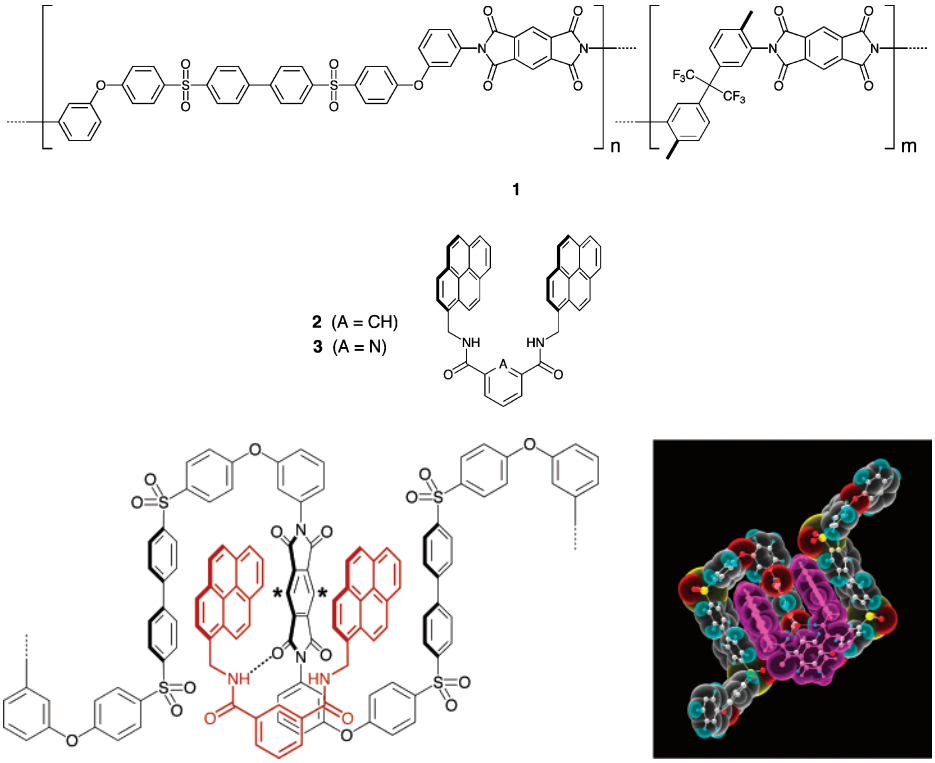

Figure 1. Molecular structure and energy-minimized model for the binding of a pyrene-based tweezer molecule to a chain-folding poly(ether-imide-sulfone) by complementary $\pi-\pi$ stacking and hydrogen bonding.

lecular chemistry have hitherto been restricted exclusively to interactions with small molecules or oligomers.

Binding of the tweezer molecule to the polyimide chain is very easily detected by ^{1}H NMR spectroscopy, because the geometry of $\pi-\pi$ stacking between the polycyclic tweezer arms and the pyromellitimide residue (Figure 1) results in a high degree of ring-current shielding of the diimide protons (starred in Figure 1) and a consequently large complexation shift (up to 2.5 ppm) of the associated resonance to higher field.[5]

Chain folding can also play a significant role in tweezer binding to polyimides by increasing the number of interatomic contacts between the polymer and the tweezer molecule, and this transforms the concept of binding from one involving simple site recognition to one in which *sequences* of monomer residues are recognized. Moreover, chain folding can lead to the imide protons experiencing a small but detectable degree of additional magnetic ring-current shielding by *adjacently* bound tweezer molecules. Thus, we have proposed that the singlet ^{1}H NMR resonance arising from these protons is shifted to higher field, not only by magnetic ring currents arising from the two pyrenyl residues of the "proximally bound" tweezer molecule but also by ring currents associated with the pyrenyl residues of *adjacent* tweezers, bound at nearest-neighbor pyromellitimide residues within the polymer chain.[5] An energy-minimized (though not unique) model in which three tweezer molecules are bound to consecutive pyromellitimide residues in a chain-folded polyimide is shown in Figure 2, with the "observed" imide protons circled in blue. The detailed theory of this proposed long-range, magnetic ring-current shielding by adjacently bound tweezer

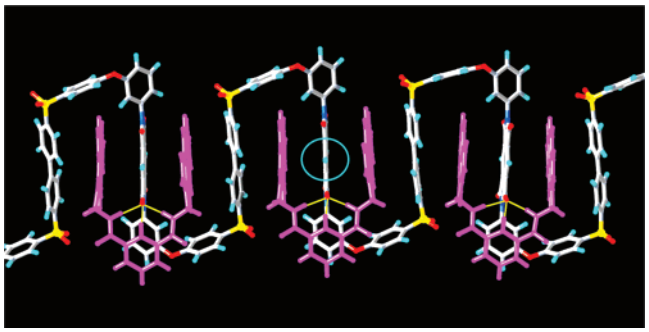

Figure 2. Energy-minimized model for adjacent binding of three tweezer molecules to consecutive pyromellitimide residues in a chain-folded poly(ether-imide-sulfone). Hydrogen bonds (N−H···O and C−H···O) between the tweezers and the polymer chain are shown in yellow and the protons subject to maximum magnetic shielding by proximally *and* adjacently bound tweezer molecules are circled in blue.

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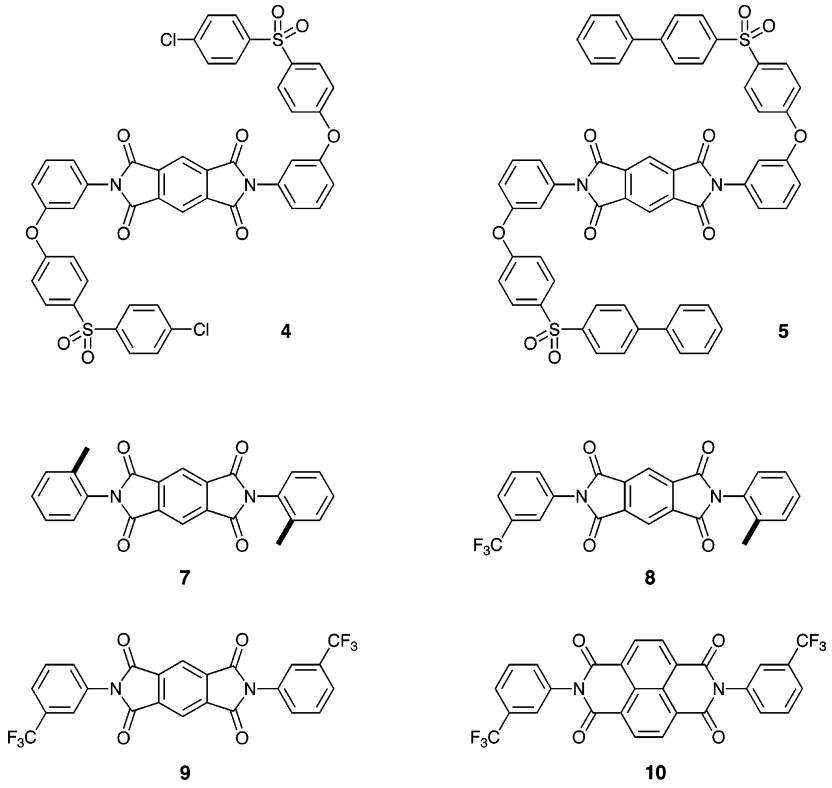
Chart 2. Model Diimides Synthesized for Tweezer-Binding Studies[a]



[a] Methyl substituents are highlighted in bold.

molecules has yet to be explored, but there is good prior evidence that such effects can be significant over the distances involved in the present supramolecular system.[11] Thus although the magnitude of aromatic ring-current shielding falls away with the distance of the proton from the aromatic ring-plane involved, recent calculations have shown that significant shielding effects (>0.1 ppm) are to be expected for benzene at H···ring−plane distances of up to 9 Å. For a *poly*cyclic aromatic, interactions between ring currents within the "shielding" molecule increase the degree of magnetic anisotropy very substantially and suggest that a pyrenyl residue could exert significant through-space proton shielding effects (>0.1 ppm) at perpendicular distances of well over 12 Å.[11] Since the perpendicular H_{imide}···pyrene separation is ca. 10.8 Å for a tweezer molecule binding at an *adjacent* imide residue in the chain-folded model shown in Figure 2, these calculations are at least consistent with the idea

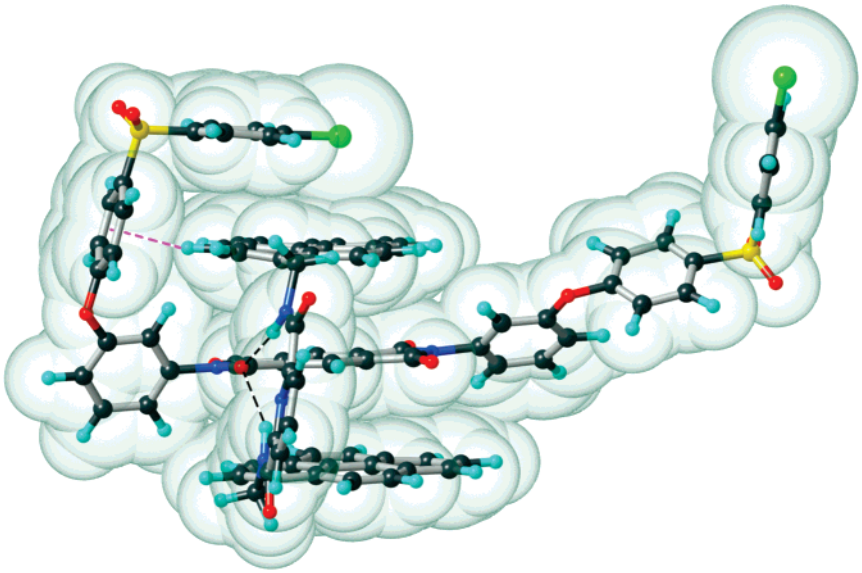


Figure 3. Single-crystal X-ray structure of the 1:1 complex **6**, formed between tweezer molecule **3** and the model imide **4**, showing chain-folding, complementary $\pi-\pi$ stacking between the pyrenyl and pyromellitimide groups, an edge-to-face CH···π contact (dashed magenta), and N−H···O hydrogen bonding (dashed black). Molecular surfaces are shown at nominal van der Waals' radii, illustrating the close steric fit between the two molecular components.

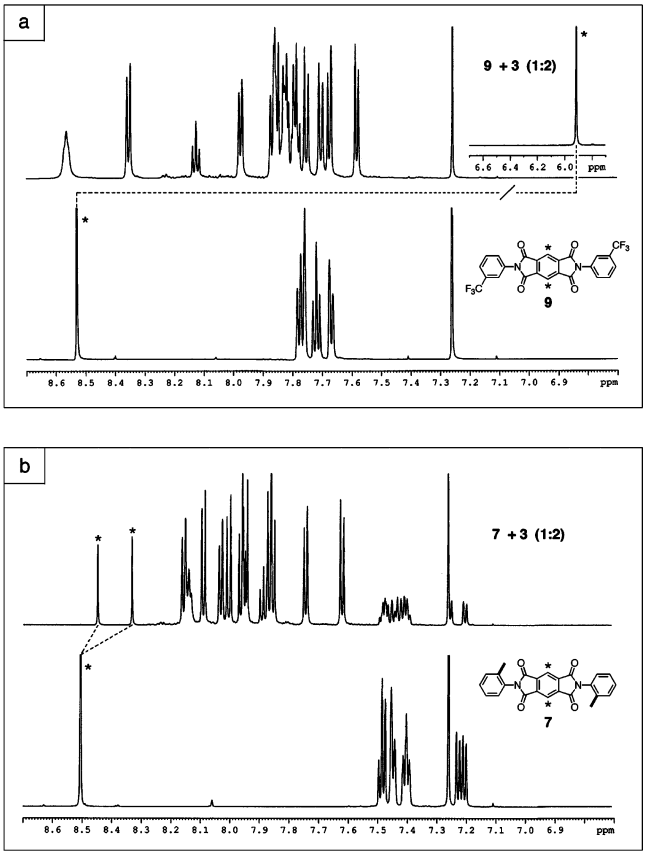


Figure 4. 700 MHz ^{1}H NMR spectra ($CDCl_3$/$(CF_3)_2CHOH$, 6:1 v/v) showing the consequences of tweezer binding (twofold molar excess of tweezer) on the spectrum of (a) the unhindered diimide **9** and (b) the doubly hindered diimide **7**. Samples were 8 mM in diimide. Diimide resonances are identified with an asterisk.

that adjacent-site binding could provide a mechanism for the tweezer's ability to act as a "sequence-selective, NMR shift reagent".

Our preliminary communications first raised the possibility of tweezer-based sequence recognition in synthetic copolymers and also of extended sequence recognition by adjacent tweezer binding.[5,6] The present paper describes new investigations designed to provide rigorous tests of this "adjacent-binding model". In particular, we have carried out detailed studies of the interactions between tweezer-type molecules and (i) a newly designed series of model diimides designed to specify, modulate, and quantify the steric environment around a pyromellitimide residue in tweezer-binding terms; (ii) a new type of copolymide containing both sterically hindered and unhindered pyromellitimide-centered sequences, which gives a clear-cut picture of the steric effects governing polymer-tweezer binding; (iii) a novel copolyimide based on an unsymmetrical diamine which restricts the range of possible diimide-centered sequences and which, again, yields a consistent but far more convincing result than that described in our initial report for a different copolymer set; and (iv) a new series of copolyimides containing both strongly binding pyromellitimide residues and entirely nonbinding hexafluoroisopropylidene−diphthalimide units.

Results and Discussion

The chain-folding models proposed for tweezer-polymer binding (Figures 1 and 2) are certainly reasonable in energetic terms and are also consistent with ^{1}H NMR data—specifically that both pyromellitimide *and* biphenylene resonances show upfield complexation shifts in the presence of tweezer molecule **2**.[5] Moreover, preliminary crystallographic studies of tweezer complexes with open-chain[6] and macrocyclic[12] oligo-imides have shown the potential of polyimide sequences to fold around and complex with the pyrenyl tweezer arms. We therefore synthesized a number of oligomeric pyromellitimide model compounds which have the potential to chain fold,[13] and attempted to crystallize complexes of these (Chart 2) with tweezer molecules **2** and **3**. However, success was achieved only with the bis-chloro-terminated oligomer **4**, which interacted with tweezer **3** to give dark red crystals of a 1:1 complex (**6**). The X-ray structure of complex **6** (Figure 3) showed that tweezer-oligomer binding occurs via (i) a double π-stacking arrangement of the electron-rich pyrenyl arms with the electron-poor pyromellitimide unit (mean imide-C-atom to pyrene-plane distances of 3.38 and 3.39 Å for the two tweezer arms), (ii) a pair of hydrogen bonds between the tweezer amide-NH protons and a pyromellitimide carbonyl oxygen (NH···O = 2.37 Å, 163°; 2.31 Å, 156°), and (iii) oligomer chain folding through ca. 180°, bringing one of its two 4-chlorophenylenesulfone residues into π-stacking contact with a pyrenyl tweezer arm (mean C-atom to pyrene-plane distance = 3.66 Å; Cl···pyrene-plane = 3.59 Å). In addition, chain folding of the oligomer results in a number of aromatic edge-to-face contacts (minimum H···C distance = 2.69 Å) which are also generally regarded as attractive interactions.[14] The second ether−sulfone unit does not fold around the tweezer in this way but, apparently for crystal-packing reasons, adopts a more extended conformation which does not allow a second complementary π-stack to be formed with the tweezer.

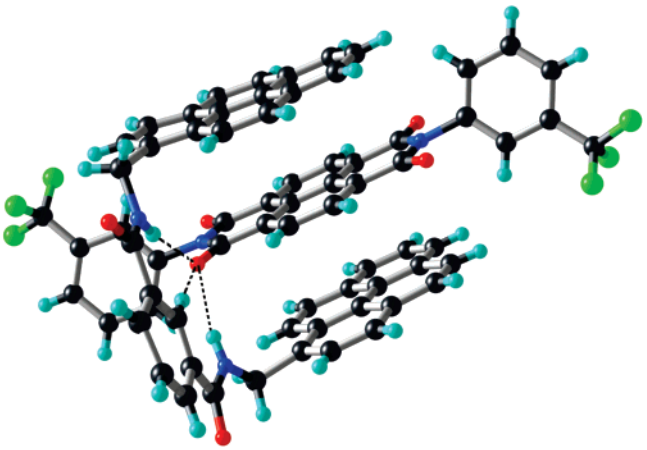


Figure 5. Single-crystal X-ray structure of the 1:1 complex (**11**) between tweezer molecule **2** and the naphthalene diimide **10**, showing complementary $\pi-\pi$ stacking and hydrogen bonding between the two components.

Computational modeling (molecular mechanics, *Cerius2*) suggested that even slight steric hindrance at the tweezer-binding site (specifically the introduction of an *o*-methyl substituent

(11) Klod, S.; Kleinpeter, E. *J. Chem. Soc., Perkin Trans.* **2001**, 1893−1898.

(12) Colquhoun, H. M.; Zhu, Z.; Williams, D. J. *Org. Lett.* **2003**, *5*, 4353−4356.

(13) The X-ray structure of the bis-H-terminated analogue of **4** shows the molecule to adopt a doubly-folded, "S"-shaped conformation in the crystal. See: O'Mahoney, C. A.; Williams, D J.; Colquhoun, H. M.; Mayo, R.; Young, S. M.; Askari, A.; Kendrick, J.; Robson, E. *Macromolecules* **1991**, *24*, 6527−6530.

(14) (a) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525−5534. (b) Carver, F. J.; Hunter, C. A.; Livingstone, D. J.; McCabe, J. F.; Seward, E. M. *Chem. Eur. J.* **2002**, *8*, 2848−2859.

adjacent to the imide nitrogen) could disrupt the high degree of shape complementarity between the two molecular components demonstrated by the close matching of van der Waals surfaces in the structure of complex **6** (Figure 3). Different association constants might therefore be expected for sterically hindered and unhindered pyromellitimide-centered sequences, potentially accounting for the sequence selectivity observed in tweezer binding.[5] To explore this idea in detail, three new model pyromellitimides (**7**, **8**, and **9**; Chart 2) containing, respectively, two, one, and zero methyl substituents ortho to the imide nitrogens were synthesized in the present work. Simple diarylpyromellitimides are often relatively insoluble, and so *m*-trifluoromethyl substituents were introduced in **7** and **8** to enhance solubility for spectroscopic studies.[15] The 1:1 association constants for complexation of tweezer molecule **3** with **7**, **8**, and **9** in chloroform/hexafluoro-propan-2-ol (6:1 v/v) were found, in the present study, to be 220, 770, and 9700 M^{-1}, respectively, as measured by the UV−visible dilution method,[16] using the respective charge-transfer absorptions at 490, 500, and 505 nm. The decrease in association constant of more than an order of magnitude between imides **9** and **8** confirms that tweezer binding is extremely sensitive to changes in the steric environment around the diimide unit and that shape-complementary recognition of the diimide site by tweezer molecule **3**, as illustrated in Figure 3, can indeed be very easily disrupted.

In keeping with the relative values of the observed association constants, tweezer-induced complexation shifts of the singlet ^{1}H NMR resonance arising from the diimide protons decreased markedly in the order **9** > **8** > **7**. As for all the tweezer-binding studies reported in this paper, fast exchange between bound and unbound tweezer molecules occurs on the NMR time scale, so that only averaged resonances are seen. Figure 4a for example shows the ^{1}H NMR spectrum of the unhindered diimide **9** (lower trace) and the corresponding spectrum in the presence of a twofold molar excess of tweezer molecule **3**. The diimide resonance shows an extremely large upfield complexation shift ($\Delta\delta$ = 2.61 ppm), but remains a sharp singlet at all tweezer concentrations, consistent with kinetically reversible but strong binding on the NMR time scale.

This is in marked contrast to the results of same experiment with the doubly hindered diimide **7** (Figure 4b), where not only is the average diimide complexation-shift more than an order of magnitude smaller than for **9**, but the resonance splits into two peaks of approximately equal intensity ($\Delta\delta$ = 0.06 and 0.18 ppm). The latter splitting must be associated with the presence of non-interconverting syn and anti isomers of compound **7**, since it is known that the steric bulk of an *o*-methyl group is sufficient to prevent free rotation about the N-aryl bond of an *N*,*N*-diarylpyromellitimide.[17] The syn isomer, with both methyl groups on the same face of the imide unit, can in principle interact weakly (via its unhindered face), with a single pyrene unit of the tweezer. In contrast, both faces of the anti isomer are blocked by methyl groups and so an even weaker interaction with the tweezer would be expected. This model

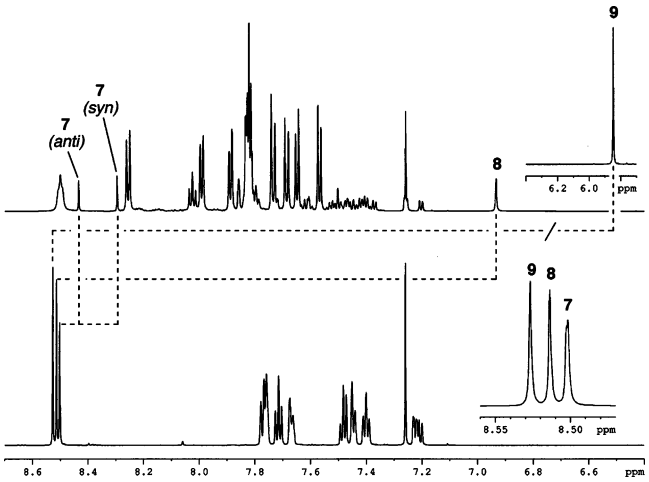
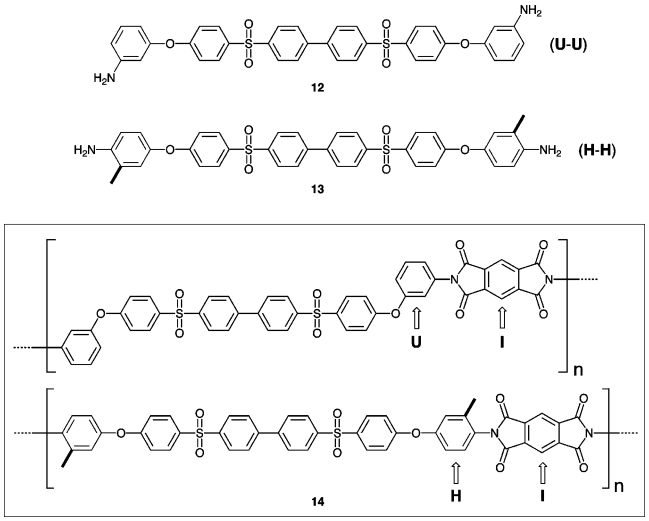


Figure 6. The 700 MHz ^{1}H NMR spectra ($CDCl_3$/$(CF_3)_2CHOH$, 6:1 v/v) of a 1:1:1 mixture of the doubly hindered, singly hindered, and unhindered diimides **7**, **8**, and **9**, respectively (lower trace), and the same mixture in the presence of a fourfold molar excess of **3** (upper trace). Complexation shifts of the pyromellitimide protons are highlighted.

Chart 3. Hindered and Unhindered Diamines and Their 1:1 Copolyimide[a]



[a] Methyl substituents are shown in bold.

predicts a slight upfield shift for the syn and an even slighter shift for the anti resonance, and the two diimide signals emerging in the presence of the tweezer molecule (Figure 4b, upper trace) can be assigned accordingly. Indeed, although the 700 MHz NMR spectrum of **7** in the *absence* of tweezer (Figure 4b, lower trace) shows only a single diimide resonance, there are more aminoaryl resonances than can be accounted for on the basis of free rotation about the C−N bonds: notably the closely spaced pair of doublets centered at ca. 7.22 ppm, assigned to the proton ortho to nitrogen in each of the two conformational isomers.

For diimide **8**, the presence of just a single *o*-methyl substituent reduces the upfield complexation shift of the diimide resonance by a factor of 2 ($\Delta\delta$ = 1.35 ppm at a 1:2 mole ratio of imide to tweezer) compared to the value of $\Delta\delta$ for the unhindered compound **9**. The absence of conformational isomerism in **8** also means that the diimide peak remains as a single resonance, even at high tweezer loadings.

Exhaustive efforts to produce diffraction-quality crystals of complexes of tweezer molecules **2** and **3** with pyromellitimides

(15) See for example: Yang, C. P.; Chen, R. S.; Chen, K. H. *Colloid Polym. Sci.* **2003**, *281*, 505−515.
(16) Nielsen, M. B.; Jeppesen, J. O.; Lau, J.; Lomholt, C.; Damgaard, D.; Jacobsen, J. P.; Becher, J.; Stoddart, J. F. *J. Org. Chem.* **2001**, *66*, 3559−3563.
(17) Shimizu, K. D.; Dewey, T. M.; Rebek, J. *J. Am. Chem. Soc.* **1994**, *116*, 5145. This paper reports a rotational barrier of ca. 30 kcal mol^{-1} for a bis(di-*ortho*)-substituted *N*,*N*′-diarylpyromellitimide.

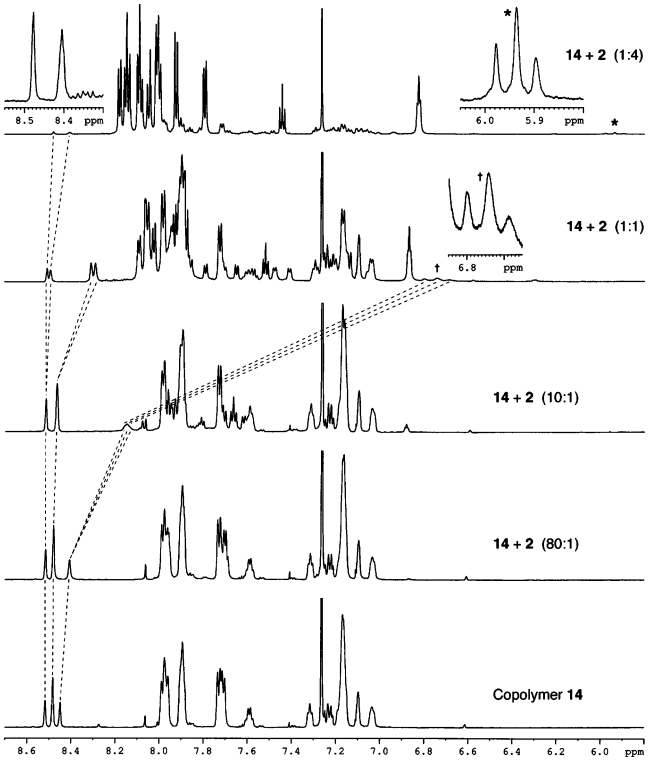


Figure 7. The 700 MHz ^{1}H NMR spectra ($CDCl_3$/$(CF_3)_2CHOH$, 6:1 v/v) of copolyimide **14** and this copolymer in the presence of 1.25, 10, 100, and 400 mol % (relative to diimide residues) of tweezer molecule **2**.

9, **8**, and (perhaps optimistically) **7** were not successful, but usable crystals of a 1:1 complex (**11**) between tweezer molecule **2** and the naphthalene−tetracarboxylic diimide **10** (a close analogue of **9**) *were* isolated. The structure of complex **11** was established by single-crystal X-ray analysis (Figure 5), despite complications arising from the presence of (i) two alternative orientations of one of the pyrenyl "tweezer arms" (only one orientation is shown), (ii) rotational disorder in the two trifluoromethyl groups, and (iii) disorder in the hexafluoropropan-2-ol solvent of crystallization. The four fused aromatic rings of the disordered pyrenyl group were refined with constrained dimensions and with occupancies x and $1 - x$, where x refined to a value of 0.61(1). The two "pyromellitimide" CF_3 groups were also disordered and two alternative positions for the three fluorine atoms in each group were refined. Constrained dimensional refinement was used for these CF_3 groups. These difficulties resulted in a relatively high value for R_1 (13.9%), but the structure of complex **11** is quite clear: the two electron-rich tweezer arms again π-stack closely with the electron-poor diimide unit (mean imide-C-atom to pyrene-plane distances of 3.46 and 3.48 Å for the two tweezer arms); the amide groups of the tweezer molecule form two hydrogen bonds converging on a single carbonyl oxygen of the diimide unit (H···O = 2.54 and 2.21 Å, NH···O = 170 and 164°); and a third hydrogen bond can be identified between this same oxygen atom and a C−H group of the isophthaloyl aromatic ring (H···O = 2.42 Å, CH···O = 173°). It is clear from this structure that the *m*-trifluoromethyl groups are directed away from the tweezer and thus do not hinder complexation to any significant extent.

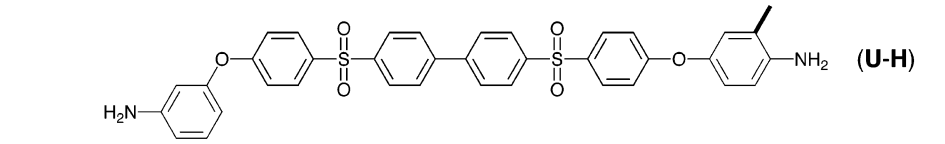
Next, an experiment was carried out in which a 1:1:1 mixture of **7**, **8**, and **9** was treated with up to a fourfold molar excess (on total imide units) of tweezer molecule **3**. As shown in Figure 6, the mixed-diimide spectrum, in the presence of **3**, corresponds closely to results obtained for the individual compounds, in keeping with fast exchange of tweezer between all three diimide substrates. This result confirmed that, in *polymeric* systems containing diimide sequences analogous to **7**, **8**, and **9**, fast exchange on the NMR time scale should enable such sequences to be readily identified through the different responses of their pyromellitimide resonances to the presence of the tweezer.

The results of these model studies implied that polyimide sequences having sterically hindering *o*-methyl groups on both aromatic rings connected directly to the pyromellitimide unit would be bound only very weakly by tweezer molecules such as **2** and **3**. Even if only one such ring were to be methylated, it seemed clear there would be a very substantial fall in the association constant relative to that of an unhindered pyromellitimide sequence. The novel 1:1 copolyimide **14** was therefore synthesized by polycondensation of pyromellitic dianhydride with diamines **12** and **13** (Chart 3), and was characterized by solution viscosimetry (η_{inh} = 0.66 dL g^{-1}), gel permeation chromatography (M_w = 87 000, M_n = 54 000), and ^{1}H NMR spectroscopy (Figure 7). Significantly, the ^{1}H NMR spectrum of this high MW copolymer showed *three* pyromellitimide resonances (δ = 8.52, 8.48, 8.45 ppm), with relative intensities 1:2:1. Since a random-sequence copolymer of this composition would contain three distinguishable imide-centered triplet sequences, namely UIU, [HIU/UIH], and HIH (HIU and UIH again being directionally degenerate) in the proportions 1:2:1, the observed resonances clearly indicated that copolymer **14** comprises a fully random system and that the resonance of relative intensity 2 represents the twofold degenerate sequence HIU/UIH. Assigning the other two diimide resonances as either UIU or HIH did not seem possible on any sort of *a priori* basis, but it was anticipated that whichever resonance was due to the unhindered, UIU, sequence would show a far greater response to the presence of tweezer molecules **2** and **3**.

In practice, the tweezer molecule **2** was selected for polymer-binding studies as its ^{1}H NMR resonances lie further upfield from the key diimide resonances than those of **3**, so reducing the extent of resonance-overlap in mixtures of the two components. Addition of only 10 mol % of **2** (relative to total pyromellitimide residues) to a 4 mM solution of polymer **14** produced a marked upfield shift (ca. 0.2 ppm) and a distinct broadening and splitting of the highest-field pyromellitimide resonance (Figure 7), identifying it as representing the sequence UIU, and, by elimination, enabling assignment of the lowest-field resonance to HIH. Progressively increasing the tweezer concentration resulted in a continued upfield shift of the UIU resonance and ultimately, at tweezer-imide ratios above 1:1, to resolution of the broadened signal into a new set of three singlet resonances with relative intensities 1:2:1 (Figure 7).

The homopolymer formed by polycondensation of pyromellitic dianhydride with the unhindered, chain-folding diamine **12** clearly contains only UIU sequences, and as a consequence shows only a singlet diimide resonance.[5] Addition of tweezer molecule **2** to this homopolymer produces essentially the same upfield shift of the diimide signal as the UIU resonance of the new copolymer **14**, but the resonance remains as a relatively sharp singlet even at very high tweezer loadings. These results confirm that, as tentatively proposed in our preliminary communications on related systems,[5,6] the tweezer-induced splitting

Chart 4. An Unsymmetrical Diamine and Its Directionally-Random Polyimide[a]



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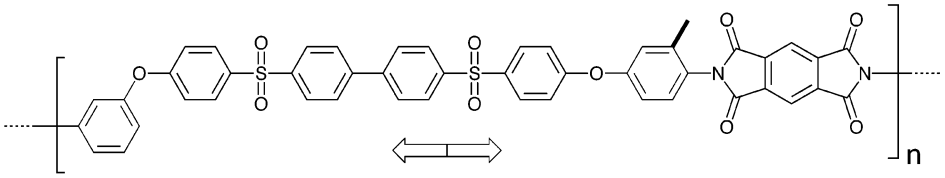


[DIRECTIONALLY RANDOM INCORPORATION OF DIAMINE **15**]

16

[a] Methyl substituents are shown in bold.

of the UIU resonance in the spectrum of copolymer **14** must arise from the recognition of *higher-order* sequence-information than that represented by a simple "triplet" of monomer residues. The present work however provides very much clearer evidence for this in that, as shown in Figure 7, ^{1}H NMR resonances assignable to *triplet* sequences (UIU, UIH, and HIH) are observed even in the absence of the tweezer.

The presence of the two different diamine residues (designated U−U and H−H, Chart 3) in copolymer **14** clearly leads to more complex sequence-patterns *when higher multiplets than triplets are considered*. Focusing just on UIU-centered sequences (since this is the triplet giving rise to the three strongly shifted imide resonances which emerge at high tweezer/imide ratios) there are four possible UIU-centered *triple*-triplets, that is, [−UIU−UIU−UIU−], [−HIU−UIU−UIU−]/[−UIU−UIU−UIH−] (the latter two sequences being directionally degenerate), and [−HIU−UIU−UIH−]. In the random, 1:1 copolymer **14**, these sequences will occur with relative probabilities 1:2:1. The splitting of the UIU resonance into three signals, with the same relative intensities, thus correlates precisely with the proportions of different triple-triplets centered on UIU.

The model-compound binding studies described above show that even a single *o*-methyl substituent adjacent to the diimide residue reduces the tweezer-binding constant by almost an order of magnitude. Thus, the difference between the above triple-triplets, from the viewpoint of tweezer binding, is that the first sequence, [−UIU−UIU−UIU−], can bind strongly to **three** tweezer molecules, while the second and third such sequences, [−HIU−UIU−UIU-]/[-UIU−UIU−UIH−], can bind only **two** and the fourth, [-HIU−UIU−UIH-], only **one** such molecule. Considering just the central pyromellitimide residue in each of these sequences, we have suggested that the binding of a tweezer molecule *adjacent* to this residue might produce a degree of additional magnetic shielding over and above the very substantial shielding provided by a tweezer bound "proximally" at the central imide unit, and that when *two* tweezers can bind adjacent to the imide being observed (one on either side, see Figure 2), a still further degree of shielding will be experienced by the central unit.[5] Thus, in the ^{1}H NMR spectra of copolymer **14** at tweezer loadings greater than 100% (Figure 7), the highest field resonance (intensity 1) can immediately be assigned to the sequence [−UIU−UIU−UIU−], the next-lowest signal (intensity 2) to the two degenerate sequences [−HIU−UIU−UIU−]/[−UIU−UIU−UIH−], and the lowest field resonance (intensity 1) to the sequence [−HIU−UIU−UIH−].

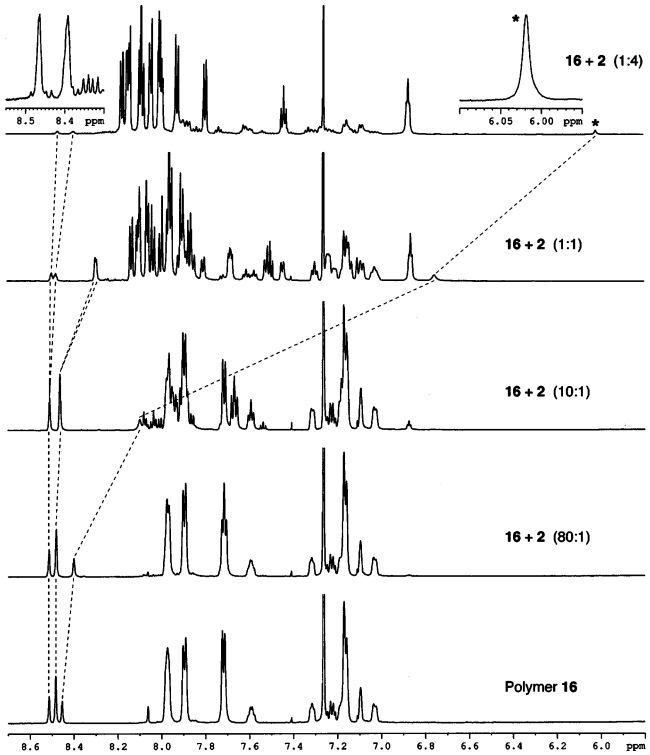
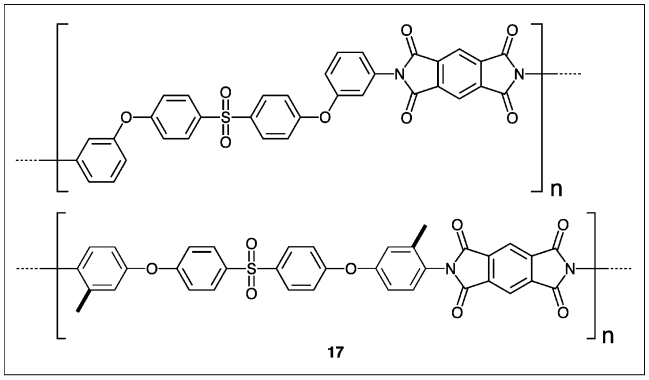


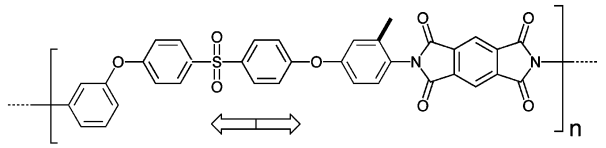
Figure 8. The 700 MHz ^{1}H NMR spectra ($CDCl_3$/$(CF_3)_2CHOH$, 6:1 v/v) of polyimide **16** and this polymer in the presence of 1.25, 10, 100, and 400 mol % (relative to diimide residues) of tweezer molecule **2**.

In molecular terms, each of these sequences actually specifies rather more than just a triple-triplet. Because each diamine residue is symmetrical, and must always be be linked to two pyromellitimide residues, the sequence [-HIU−UIU−UIH-] for example actually defines the longer sequence [-IH−HIU−UIU−UIH-HI-]. Such a sequence (like all four possible sequences of this type) comprises no fewer than 29 aromatic rings linked variously by ether, sulfone, imide and biphenylene linkages, and yet it is represented unambiguously in Figure 7 by just a single NMR peak. In a very real sense, the tweezer molecule "reads" this extended sequence-information through its ability to bind rapidly and reversibly at adjacent or indeed nonadjacent

Chart 5. Polyimides Derived from Short-Chain, Nonfolding Diamines[a]



17



18

[a] Methyl substituents are shown in bold.

positions on the polymer chain, and "reports" it through the additive effects of pyrenyl ring-current shielding on the chemical shift of the diimide protons.

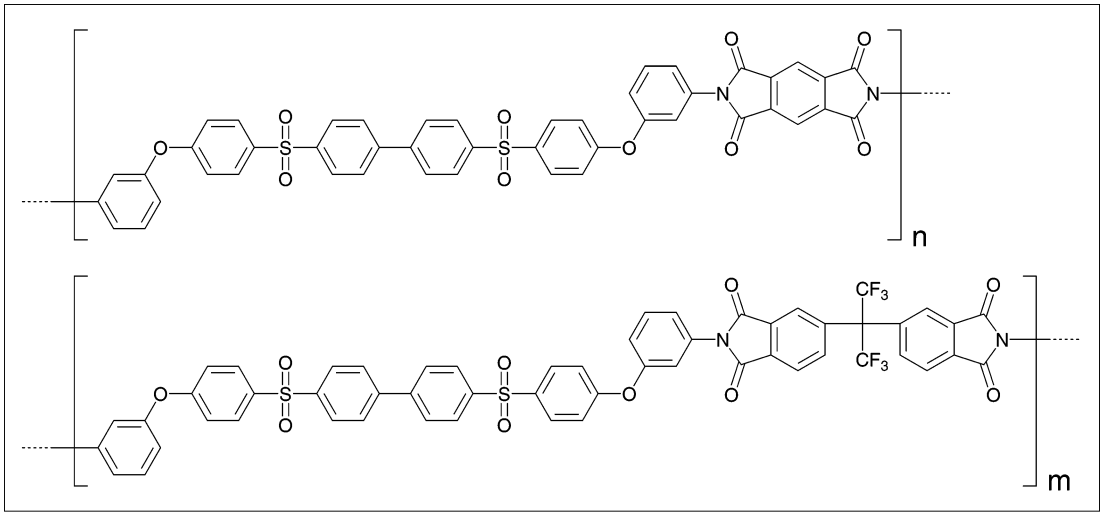
To further validate the adjacent-binding model, we next designed a new polyimide (**16**), which is isomeric with **14**, but in which every pyromellitimide-centered sequence *adjacent* to the sequence UIU is sterically hindered by at least one *o*-methyl substituent. The greatly weakened tweezer binding at all diimide sites adjacent to UIU should then result in little or no tweezer-induced splitting of the UIU resonance. The latter should however still respond to the presence of a *proximally* bound tweezer molecule in terms of a substantial upfield shift.

Polymer **16** (Chart 4) was obtained by polycondensation of the novel, unsymmetrical diamine **15** with pyromellitic dianhydride, and showed $\eta_{inh} = 0.61$ dL g^{-1}, $M_w = 67\,000$, and $M_n = 46\,000$. Assuming that incorporation of **15** into the polyimide chain is directionally random, the triplet sequences UIU, UIH/HIU, and HIH should again be present with relative probabilities 1:2:1. However, because of the unsymmetrical nature of diamine **15** ("U−H"), the UIU-centered triple-triplet sequences which can be present in this polymer must *all* contain at least two hindering *o*-methyl groups. The possible sequences are thus [−UIH−UIU−HIU−], [−HIH−UIU−HIU−]/[-UIH−UIU−HIH-] (the latter being directionally degenerate), and [−HIH−UIU−HIH−].

The ^{1}H NMR spectrum of polymer **16** (Figure 8) closely resembles that of **14**, and again shows three resonances (intensities 1:2:1) in the diimide region, with the highest-field signal assignable to the triplet UIU (on the basis of the results for copolymer **14**). Progressive addition of tweezer molecule **2** to a solution of polymer **16** resulted in the latter signal shifting strongly upfield, confirming its assignment to UIU, but as predicted by the model developed above for steric inhibition of adjacent binding and demonstrated in Figure 8, *no splitting of this resonance was observed*, even at very high tweezer loadings (up to 400 mol % of tweezer to imide). This experiment provides conclusive evidence that (a) the splitting of the UIU resonance for polymer **14** into three signals in the presence of tweezer molecule **2** is indeed due to tweezer binding at one, two, or three adjacent pyromellitimide residues on the polymer chain and that (b) such binding is strongly inhibited by only a single, neighboring *o*-methyl group, to the extent that tweezer binding adjacent to the strongly binding sequence UIU becomes undetectable in terms of its influence on the chemical shift of the UIU diimide resonance.

It should be emphasized that the present comparison, between polyimides based on *chain-folding* diamines with symmetrical and unsymmetrical substitution patterns, affords a very much more clear-cut result than that reported in our preliminary communication where simpler, non-chain-folding diamines were studied (Chart 5).[6] In that study, the polyimide (**18**) based on an unsymmetrical diamine certainly showed no splitting of the diimide resonance in the presence of the tweezer, but the splitting of this resonance in the corresponding copolymer (**17**) based on symmetrical, short-chain monomers was only *just* detectable and did not increase at high tweezer loadings. This difference provides further evidence for the chain-folded

Chart 6. Copolyimides Derived from Hexafluoroisopropylidene-diphthalic Dianhydride.



19 (m = n), **20** (m = 2n)

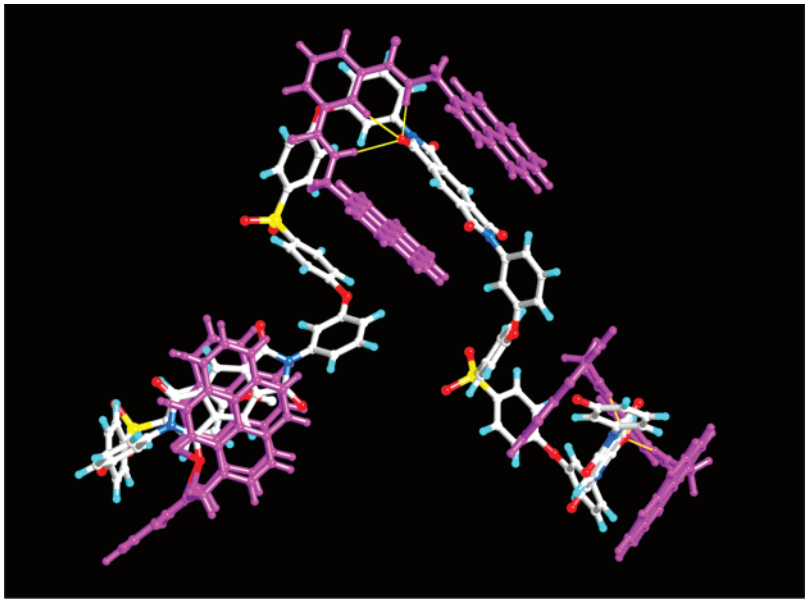


Figure 9. Energy-minimized model for adjacent binding of three tweezer molecules to consecutive pyromellitimide residues in the nonfolding poly(ether-imide-sulfone) **17** (Chart 5). Hydrogen bonds (N−H···O and C−H···O) between the tweezers and the polymer chain are shown in yellow.

adjacent-binding model illustrated in Figure 2, where the adjacently bound tweezer molecules clearly lie in the optimum orientation to produce maximum additional magnetic ring-current shielding of the central diimide protons. Mutual orientation of this type is clearly impossible in the "nonfolding" system described previously,[6] as demonstrated by an energy-minimized model for triply adjacent tweezer binding in the short-chain system (Figure 9) which shows the pyrenyl planes of adjacent tweezer molecules to be more nearly orthogonal than parallel.

In the ^{1}H NMR spectra of both **14** and **16**, the "HIH" diimide resonance undergoes tweezer-induced splitting, giving two resonances assigned (as for the model diimide **7**) to syn and anti conformations of the bis(*o*-methylphenylene)pyromellitimide unit, now within a polymer chain. Interestingly however, the "HIU" resonance which remains a singlet in the monomeric diimide **8**, also splits to give two resonances in the spectra of both polyimides (Figures 7 and 8) though the effect is more marked for copolymer **14**. The fact that such splitting is observed only for polymeric systems implies that, once again, sequence information of a higher order than the simple HIU triplet is being detected by the tweezer. Enumeration of all possible HIU-centered triple-triplets for both **14** and **16** reveals that, in each case there are equal populations of HIU triplets *with* and *without* the strongly binding UIU triplet adjacent to the observed resonance, so that the twofold splitting of the HIU resonance can be assigned to the occurrence—or nonoccurrence—of strong tweezer binding adjacent to an "observed" site *which is itself only very weakly bound by the tweezer*. Curiously, the effects of tweezer binding adjacent to nonbound diimide centers are more pronounced in the ^{1}H NMR spectra of polyimides **17** and **18**, despite the absence of chain folding. This particular effect may be enhanced by the inherently shorter dynamic distance between pyromellitimide residues in these polymers, but it seems clear that at this point the limits of qualitative interpretation have been reached. In particular, the extent to which polymer chain conformations are themselves *modified* by dynamic tweezer binding, with the resulting possibility of co-operativity in binding, is as yet unknown. More quantitative computational

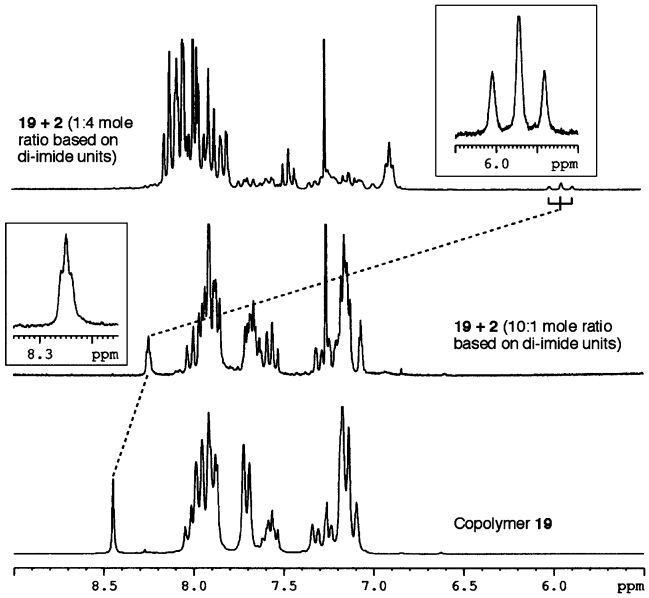


Figure 10. ^{1}H NMR spectra (250 MHz) showing the consequences of increasing the proportion of tweezer molecule **2** relative to the pyromellitimide content of copolymer **19**.

modeling studies of adjacent tweezer binding and magnetic ring-current effects in these polyimide systems are however currently in progress.

In the present work, a new and definitive test of the adjacent binding model involved the synthesis of a further set of novel copolymers, **19** and **20** (Chart 6), based on diamine **12** but now containing both pyromellitimide and hexafluoroisopropylidene-diphthalimide residues. It seemed highly unlikely that the latter units would act as target sites for tweezer binding, being non-coplanar, bulky, and having only two electron-withdrawing carbonyl groups per aromatic ring. The only function of this monomer residue in the context of tweezer binding would thus be to *disrupt* consecutive sequences of pyromellitimide residues, thereby isolating these residues as singlets, doublets, triplets, and higher adjacent multiplets. The adjacent-binding model

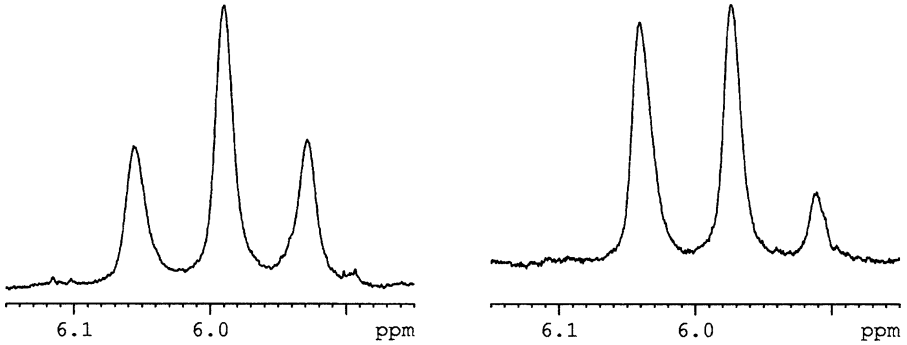


Figure 11. Pyromellitimide resonances of copolymers **19** (left) and **20** (right) in the presence of a fourfold molar excess (per diimide unit) of tweezer molecule **2**. Relative probabilities of the sequences SFSISFS, [SISISFS + SFSISIS], and SISISIS in these copolymers are calculated to be 1:2:1 and 4:4:1, respectively, in very good agreement with the observed intensities.

would then predict that, in copolymers **19** and **20**, *all* pyromellitimide residues would be bound strongly by tweezer molecule **2**, but that where adjacent binding is possible (i.e., in consecutive sequences of two or three pyromellitimide residues), the additional ring-current shielding should lead to increased values $\Delta\delta$ for the corresponding ^{1}H NMR resonances.

In practice, the pyromellitimide singlet resonance moves steadily upfield as the tweezer/imide mole ratio increases, but above a ratio of ca. 1:10, this resonance broadens and begins to split quite definitely into three peaks. At higher tweezer/imide ratios, this resonance becomes lost in a dense cluster of aromatic signals, but, when the tweezer/imide ratio reaches 2:1, it re-emerges upfield of all other aromatic resonances as a clear set of three signals with relative intensities 1:2:1 (Figure 10). The pattern sharpens and narrows slightly, but is otherwise maintained, as the three resonances continue to move to higher field with increasing tweezer/imide ratio.

Labeling the residues derived from the sulfone-based diamine **12** as "S", pyromellitimide units as "I" and hexafluoroisopropylidenediphthalimide residues as "F", copolymers **19** and **20** contain four possible SIS-centered tris-diimide sequences, that is, [−SISISIS−], [−SFSISIS−]/[−SISISFS−] (the latter two sequences being directionally degenerate), and [−SFSISFS−]. These sequences allow tweezer binding at one, two, and three adjacent pyromellitimide sites, respectively, and in the random, 1:1 copolymer **19**, they occur with relative probabilities 1:2:1. The splitting of the SIS resonance into three peaks, with these same relative intensities, thus correlates precisely with the proportions of different tris-diimide sequences centered on SIS.

A simple but important check on this interpretation involved varying the proportions of comonomers in the polymer, since the statistical proportions of the different sequences then change in a quantitatively predictable manner. Random copolymer **20**, based now on a 1:2 mole ratio of the two dianhydrides, thus contains the above tris-diimide sequences in proportions 1:4:4, respectively, rather than in the 1:2:1 ratio for 1:1 copolymer **19**. As shown in Figure 11, the intensities of the three diimide resonances observed for copolymers **19** and **20** at high tweezer loadings match the predicted ratios very closely indeed.

Conclusions

The encoding and readout of digital sequence-information at the molecular level, as achieved in biological systems, represents a major current challenge for synthetic and supramolecular polymer chemistry. In the present paper we have shown that even apparently minor changes in the steric environment around a pyromellitimide residue in an aromatic copolyimide can result in more than an order of magnitude variation in binding constant for a molecular tweezer. As a result, the information represented by monomer sequences up to 29 aromatic rings in length can be readily detected by the tweezer and reported through the cumulative ring-current shielding effects of adjacent tweezer binding on the ^{1}H NMR chemical shifts of the corresponding diimide residues. This cumulative ring-current model was validated by two novel and conceptually different experimental approaches. One involved a polyimide derived from an *unsymmetrical* diamine, in which the sequence-distribution inhibits *adjacent* tweezer binding. Here, as predicted by the model, tweezer-induced splitting of the ^{1}H NMR pyromellitimide resonance is no longer observed, consistent with tweezer binding being "switched off" by even relatively slight steric hindrance around the adjacent diimide binding site. The second approach involves tweezer binding to copolymers in which there are *no* sterically hindered pyromellitimide residues, but in which consecutive sequences of such residues are simply disrupted by different, nonbinding diimide units, generating a chemically distinct type of sequence information which is once again very easily detected by the tweezer molecule.

Experimental Section

Materials and Methods. Synthetic procedures were performed under an atmosphere of dry nitrogen unless otherwise specified. Commercial solvents and reagents were used without purification unless otherwise stated. *N*,*N*-dimethylacetamide (DMAc) was distilled over calcium hydride before use. Compounds **2**,[18] **3**,[18] **4**,[6] and **12**[19] were prepared according to literature procedures. Proton and ^{13}C NMR spectra were recorded on Bruker AV-700 and DPX-250 MHz spectrometers. Single-crystal X-ray data for **6** were measured using Mo Kα radiation on a Bruker-Nonius Kappa CCD diffractometer at 120 K and for **11** on an Oxford Diffraction X-Calibur CCD diffractometer using Cu Kα radiation at 150 K. Full details of the data collections, structure solutions, and refinements are given below and in the Supporting Information. Details of other instrumentation and analytical techniques are given as Supporting Information.

Synthetic Procedures. Syntheses of novel diimides and polyimides are given below. Synthetic procedures for new monomers and intermediates are described in the Suppporting Information.

Model Diimides 5, **7**, **9**, and **10**. The synthesis of **9** is given as an example. A solution of 3-trifluoromethyl aniline (1.933 g, 12 mmol) and pyromellitic dianhydride (0.654 g, 3 mmol) was heated to reflux

(18) Colquhoun, H. M.; Zhu, Z.; Williams, D. J. *Org. Lett.* **2003**, *5*, 4353−4356.
(19) Colquhoun, H. M.; Williams, D. J.; Zhu, Z. *J. Am. Chem. Soc.* **2002**, *134*, 13346−13347.

in dry DMAc (30 mL) under nitrogen for 16 h. The clear, pale yellow solution was concentrated to ca. 5 mL and cooled to room temperature. The yellow crystals were filtered off, washed with DMAc (2 mL) and methanol (10 mL), and dried at 100 °C for 2 h to afford **9** as a crystalline yellow solid.

Diimide 5. Yield 0.6 g, 54%; mp 356 °C. ^{1}H NMR ($CDCl_3$/hexafluoropropan-2-ol 6:1 v/v, 250 MHz) δ 8.46 (s, 2H), 7.93 (d, J = 8.6 Hz, 4H), 7.89 (d, J = 8.9 Hz, 4H), 7.75 (d, J = 8.6 Hz, 4H), 7.61 (t, J = 8.1 Hz, 2H), 7.58 (d, J = 8.6 Hz, 4H), 7.51 − 7.44 (m), 7.30 (dd, J = 8.1 and 2.1 Hz, 2H), 7.20 (dd, J = 8.1 and 2.1 Hz, 2H), 7.17(d, J = 8.9 Hz, 4H), 7.16 (t, J = 2.1 Hz, 2H). ^{13}C NMR ($CDCl_3$/hexafluoropropan-2-ol 6:1 v/v, 62.5 MHz) δ 165.7, 162.2, 156.0, 147.5, 139.2, 138.8, 137.4, 134.6, 132.1, 131.5, 130.2, 129.5, 129.2, 128.6, 128.1, 127.7, 123.2, 121.3, 120.1, 118.9, 118.7. IR (Nujol): 1723 (imide νC═O), 1375 (νC−N), 1243 (νC−O−C), 1160, 901, 848 and 835 cm^{-1}. MS (MALTI-TOF): m/z = 1007 $[M + Na]^+$. Anal. Calcd for $C_{58}H_{36}N_2O_{10}S_2$: C, 70.72; H, 3.68; N, 2.84%. Found: C, 70.72; H, 3.59; N, 2.94%.

Diimide 7. Yield 1.01 g, 85%; mp 398 °C. ^{1}H NMR ($CDCl_3$/hexafluoropropan-2-ol 6:1 v/v, 700 MHz) δ 8.51 (s, 2H), 7.49 (t, J = 7.7 Hz, 2H), 7.45 (d, J = 7.7 Hz, 2H), 7.40 (t, J = 7.7 Hz, 2H), 7.23 (d, J = 7.7 Hz, 1H), 7.21 (d, J = 7.7 Hz, 1H), 2.21 (s), 2.20 (s). ^{13}C NMR ($CDCl_3$/hexafluoropropan-2-ol 6:1 v/v, 62.5 MHz) δ 166.4, 137.7, 136.8, 132.0, 131.0, 129.4, 128.6, 127.8, 120.2, 17.7. IR (Nujol): 1729 (imide νC═O), 1371 (νC−N), 757 and 726 cm^{-1}. MS (CI): m/z = 396 $[M]^+$. Anal. Calcd for $C_{24}H_{16}N_2O_4$: C, 72.72; H, 4.07; N, 7.07%. Found: C, 72.70; H, 4.02; N, 7.16%.

Diimide 9. Yield 1.12 g, 74%; mp 326 °C. ^{1}H NMR ($CDCl_3$/hexafluoropropan-2-ol 6:1 v/v, 700 MHz) δ 8.53 (s, 2H), 7.79 (d, J = 7.9 Hz, 2H), 7.76 (s, 2H), 7.72 (t, J = 7.9 Hz, 2H), 7.67 (d, J = 7.9 Hz, 2H). ^{13}C NMR ($CDCl_3$/hexafluoropropan-2-ol 6:1 v/v, 62.5 MHz) δ 165.7, 137.4, 132.9, 132.4, 131.2, 130.6, 130.0, 126.4, 124.0, 120.3. IR (Nujol): 1713 (imide νC═O), 1391 (νC−N), 900, 840, and 797 cm^{-1}. MS (CI): m/z = 504 $[M]^+$. Anal. Calcd. for $C_{24}H_{10}F_6N_2O_4$: C, 57.16; H, 2.00; N, 5.55%. Found: C, 57.08; H, 1.99; N, 5.55%.

Diimide 10. Yield 1.0 g, 60%; mp 344 °C. ^{1}H NMR ($CDCl_3$/hexafluoropropan-2-ol 6:1 v/v, 250 MHz) δ 8.87 (s, 2H), 7.86 (d, J = 7.9 Hz, 2H), 7.76 (t, J = 7.9 Hz, 2H), 7.63 (s, 2H), 7.54 (d, J = 7.9 Hz, 2H). ^{13}C NMR ($CDCl_3$/hexafluoropropan-2-ol 6:1 v/v, 62.5 MHz) δ 163.9, 134.6, 133.3, 132.8, 132.6, 132.1, 130.9, 127.5, 127.1, 125.9, 125.8, 121.5. IR (Nujol): 1712 (imide νC═O), 1378 (νC−N), 1160, 775, and 742 cm^{-1}. MS (CI): m/z = 554 $[M]^+$. Anal. Calcd for $C_{28}H_{12}F_6N_2O_4$: C, 60.66; H, 2.18; N, 5.05%. Found: C, 60.44; H, 2.10; N, 4.97%.

Unsymmetrical Diimide 8. A mixture of pyromellitic dianhydride (3.27 g, 15 mmol) and *o*-toluidine (1.61 g, 15 mmol) in dry DMAc (200 mL) was stirred at room temperature under nitrogen for 0.5 h. Then 3-(trifluoromethyl)aniline (2.90 g, 18 mmol) was added. The reaction mixture was heated for 16 h, cooled, precipitated in water, filtered, dried at 100 °C for 2 h, and purified by chromatography (dichloromethane/hexane 1:1) followed by four crystallizations from chloroform. Yield 0.48 g, 7.0%; mp 267 °C. ^{1}H NMR ($CDCl_3$/hexafluoropropan-2-ol 6:1 v/v, 700 MHz) δ 8.52 (s, 2H), 7.78 (d, J = 7.9 Hz, 1H), 7.76 (s, 1H), 7.72 (t, J = 7.9 Hz, 1H), 7.67 (d, J = 7.9 Hz, 1H), 7.49 (t, J = 7.7 Hz, 1H), 7.45 (d, J = 7.7 Hz, 1H), 7.41 (t, J = 7.7 Hz, 1H), 7.23 (d, J = 7.7 Hz, 1H), 7.21 (d, J = 7.7 Hz, 1H), 2.20 (d, J = 7.8 Hz, 3H). ^{13}C NMR ($CDCl_3$/hexafluoropropan-2-ol 6:1 v/v, 62.5 MHz) δ 165.6, 137.4, 132.9, 132.4, 131.2, 130.6, 130.0, 126.4, 120.3, 17.7. IR (Nujol): 1719 (imide, νC═O), 1377 (νC−N), 900, 837, and 766 cm^{-1}. MS (CI): m/z = 450 $[M]^+$. Anal. Calcd for $C_{24}H_{13}F_3N_2O_4$: C, 64.00; H, 2.91; N, 6.22%. Found: C, 63.74; H, 2.73; N, 6.18%.

Synthesis of Polyimides. The synthesis of polyimide **14** is given as an example. Diamines **12** (0.324 g, 0.5 mmol) and **13** (0.338 g, 0.5 mmol) were dissolved in DMAc (4 mL) by stirring at room temperature, and when the diamines had dissolved completely pyromellitic dianhydride (0.218 g, 1 mmol) was added in one portion. The dianhydride gradually dissolved and the mixture became viscous after 0.5 h. The pale yellow viscous solution was stirred for a further 20 h, then transferred to a Petri dish and heated at 80 °C under vacuum for 2 h to remove the solvent. The resulting film of polyamic acid was imidized by heating sequentially at 120 °C for 10 min, 150 °C for 10 min, 180 °C for 10 min, 210 °C for 10 min, and finally at 250 °C for 30 min. The polyimide film was dissolved in DMF and reprecipitated twice in methanol to give uniform beads of polyimide **14** which were dried at 80 °C for 4 h.

Polyimide 14. Yield, 0.81 g, 96%; T_g = 313 °C, η_{inh} = 0.66 dL g^{-1}; M_n = 54000, M_w = 87000. ^{1}H NMR ($CDCl_3$/hexafluoropropan-2-ol 6:1 v/v, 700 MHz) δ 8.52 (s), 8.48 (s), 8.45 (s), 7.99−7.96 (m), 7.89 (br), 7.73−7.70 (m), 7.60−7.57 (m), 7.32 (br), 7.23−7.21 (m), 7.17 (br), 7.10 (br), 7.06 (br), 2.36 (s). ^{13}C NMR ($CDCl_3$/hexafluoropropan-2-ol 6:1 v/v, 62.5 MHz) δ 166.2, 165.6, 162.3, 156.7, 155.8, 144.8, 141.0, 139.5, 137.6, 137.4, 134.4, 132.4, 131.5, 130.6, 130.4, 128.5, 128.4, 126.1, 123.3, 123.1, 119.1, 118.8, 18.1. IR (film from DMF): 1779, 1729 (imide νC═O), 1375 (νC−N), 1246 (νC−O−C), 1107, 728 cm^{-1}.

Polyimide 16. Yield, 0.28 g, 88%; T_g = 308 °C, η_{inh} = 0.61 dL g^{-1}; M_n = 46000, M_w = 67000. ^{1}H NMR ($CDCl_3$/hexafluoropropan-2-ol 6:1 v/v, 700 MHz) δ 8.51 (s), 8.48 (s), 8.45 (s), 7.97 (br), 7.90 (d, J = 8.2 Hz), 7.72 (d, J = 8.0 Hz), 7.60−7.57 (m), 7.32 (br), 7.24−7.21 (m), 7.17−7.16 (m), 7.10 (br), 7.04 (br), 2.36 (s). ^{13}C NMR ($CDCl_3$/hexafluoropropan-2-ol 6:1 v/v, 62.5 MHz) δ 166.2, 165.7, 162.4, 156.7, 155.8, 144.8, 140.9, 139.5, 137.6, 137.4, 134.4, 132.3, 131.5, 130.6, 130.4, 128.5, 128.4, 126.1, 123.3, 123.1, 119.1, 118.8, 18.1. IR (film from DMF): 1779, 1729 (imide νC═O), 1375 (νC−N), 1246 (νC−O−C), 1107, 728 cm^{-1}.

Copolyimide 19. Yield, 90%, T_g = 273 °C, η_{inh} = 0.74 dL g^{-1}; M_n = 68.4 × 10^3 daltons; M_w = 109 × 10^3 daltons (polystyrene standards). ^{1}H NMR ($CDCl_3$/hexafluoro-propan-2-ol 6:1 v/v, 700 MHz): δ = 8.44 (s), 8.06 (s), 8.01 (d, J = 8.0 Hz), 7.95 (m), 7.88 (m), 7.70 (br), 7.57 (m), 7.31 (d, J = 7.9 Hz), 7.23 (d, J = 8.0 Hz), 7.16 (m), 7.07 (s) ppm. ^{13}C NMR ($CDCl_3$/hexafluoro-propan-2-ol 6:1 v/v, 62.5 MHz): δ = 167.3, 167.1, 165.7, 162.3, 155.9, 144.8, 140.8, 140.2, 137.4, 137.0, 134.3, 134.2, 132.5, 132.4, 132.3, 132.1, 130.4, 128.9, 126.0, 124.9, 123.5, 123.3, 121.2, 121.0, 120.0, 118.9 ppm. IR (film from DMF): 1779, 1729 (imide, νC═O), 1375 (νC−N), 1249 (νC−O−C), 1106, 725 cm^{-1}.

Copolyimide 20. Yield, 86%, T_g = 276 °C, η_{inh} = 0.41 dL g^{-1}; M_n = 9.3 × 10^3 daltons; M_w = 23.2 × 10^3 daltons (poly(ethylene glycol). ^{1}H NMR ($CDCl_3$/hexafluoro-propan-2-ol, 6:1 v/v, 250 MHz) δ = 8.45 (s), 7.95 (m), 7.71 (d, J = 8.0 Hz), 7.57 (m), 7.32 (d, J = 8.4 Hz), 7.24 (d, J = 8.2 Hz), 7.17 (m), 7.09 (br) ppm. ^{13}C NMR ($CDCl_3$/hexafluoro-propan-2-ol 6:1 v/v, 62.5 MHz): δ = 167.4, 167.2, 165.7, 162.4, 155.9, 144.9, 140.8, 140.2, 137.4, 137.0, 134.2, 132.4, 132.2, 132.1, 131.5, 130.4, 128.9, 128.5, 128.4, 128.3, 125.9, 124.9, 123.5, 123.4, 121.3, 120.0, 118.9 ppm. IR (film from DMF): 1779, 1728 (imide, νC═O), 1373 (νC−N), 1246 (νC−O−C), 1107, 725 cm^{-1}.

X-ray Crystallography. Single crystals of complex **6** were grown by vapor diffusion of an equimolar solution of the two components in chloroform/hexafluoropropan-2-ol (6/1 v/v) with diethyl ether as nonsolvent. Crystal data for **6**: $C_{87}H_{53}Cl_2N_5O_{12}S_2 \cdot 3C_3H_2F_6O \cdot CHCl_3$ M_r = 2118.9, triclinic, $P\bar{1}$, a = 10.9503(4), b = 17.6840(10), c = 23.9264-(12) Å, α = 104.520(2), β = 96.031(3), γ = 91.682(3)°. V = 4452.9-(4) Å^3, T = 120(2) K, Z = 2, D_c = 1.58 g cm^{-3}, μ (Mo Kα) = 0.32 mm^{-1}, F (000) = 2152. Independent measured reflections 9168. R_1 = 0.139, wR_2 = 0.391 for 6742 independent observed reflections [$2\theta \leq$ 20.8°, $I > 2\sigma(I)$]. Average $I/\sigma(I)$ 15.5. CCDC 248234. Crystals of **11** were grown by vapor diffusion of an equimolar solution of the two components in chloroform/hexafluoropropan-2-ol (6/1 v/v) with hexane as nonsolvent. Crystal data for **11**: $C_{70}H_{40}F_6N_4O_6 \cdot 4C_3H_2F_6O \cdot H_2O$ M_r = 1837.3, monoclinic, $P2_1/c$, a = 14.688(17), b = 25.33(3), c = 20.85-(2) Å, β = 101.701(10)°. V = 7596(15) Å^3, T = 150(2) K, Z = 4, D_c

$= 1.61$ g cm^{-3}, μ (Cu Kα) $= 1.4$ mm^{-1}, F (000) $= 3712$. Independent measured reflections 11888. $R_1 = 0.139$, $wR_2 = 0.386$ for 7502 independent observed reflections [$2\theta \leq 130°$, $I > 2\sigma(I)$]. Average $I/\sigma(I)$ 27.4. CCDC 656876.

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Supporting Information Available: Instrumentation and analytical techniques; synthetic procedures for monomers and intermediates; crystallographic data in CIF format for **6** and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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