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Convergent Synthesis of Nonsymmetric π-Stacked Protophanes Assembled with Urea Linkers

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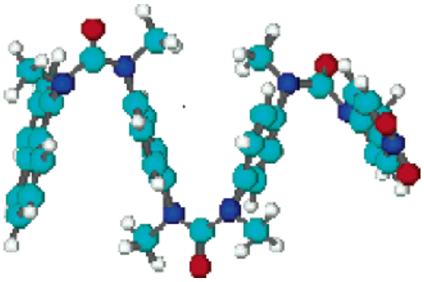

A convergent approach has been developed for the preparation of nonsymmetric tertiary arylureas possessing two or three urea linkages. This approach has been used for the preparation of ureas possessing 1-naphthylenyl and 4-nitrophenyl end groups separated by either one or two phenylene diamine bridging units. These ureas were constructed as prototypes for donor−bridge−acceptor systems based on tertiary arylurea architecture. AM1 calculations indicate a preference of these arylureas for folded, protophane structures in which the aryl groups are loosely π-stacked. Analysis of the ^{1}H NMR chemical shifts supports the assignment of folded structures in solution. The absorption and luminescence spectra of tertiary ureas possessing 1-naphthylenyl and/or 4-nitrophenyl are reported. The absence of fluorescence and appearance of structured phosphorescence at 77 K are attributed to nitrophenyl-localized lowest energy singlet and triplet states. Localization of excitation on the acceptor chromophore precludes investigation of charge transfer in these systems.

Introduction

Electronic interactions between aromatic chromophores have been extensively investigated in linear (extended) donor−bridge−acceptor (DBA) systems.[1] Recently, electronic interactions involving the π-stacked base pairs in duplex DNA have become the subject of intense interest.[2] Synthetic π-stacked DBA systems offer potential advantages over DNA, including synthetic control and solubility in nonaqueous solvents. Despite these advantages synthetic π-stacked DBA systems have received relatively little attention. During the 1970s the arduous synthesis of multilayer DBA paracyclophanes was accomplished by Staab and Misumi and their co-workers.[3,4] However, the nature of the electronic interactions in these fascinating molecules was not extensively investigated. Recently, Therien and co-workers[5] have reported the synthesis of rigid π-stacked porphyrin−phenylene−quinone DBA systems possessing one or two phenylenes constructed using 1,8-disubstituted naphthalenes as the scaffold. Similarly, Napper et al.[6] have used a rigid polycyclic scaffold to assemble a loosely π-stacked DBA system. Such singly bridged π-stacked systems have been referred to as "protophanes".[4]

Our interest in arylurea-based protophane systems was prompted by reports of the intrinsic cis,cis-preference of *N*,*N*′-dimethyl-*N*,*N*′-diphenylurea and homologues with as many as five π-stacked benzene or 9 π-stacked naphthalene rings.[7] We have previously reported the

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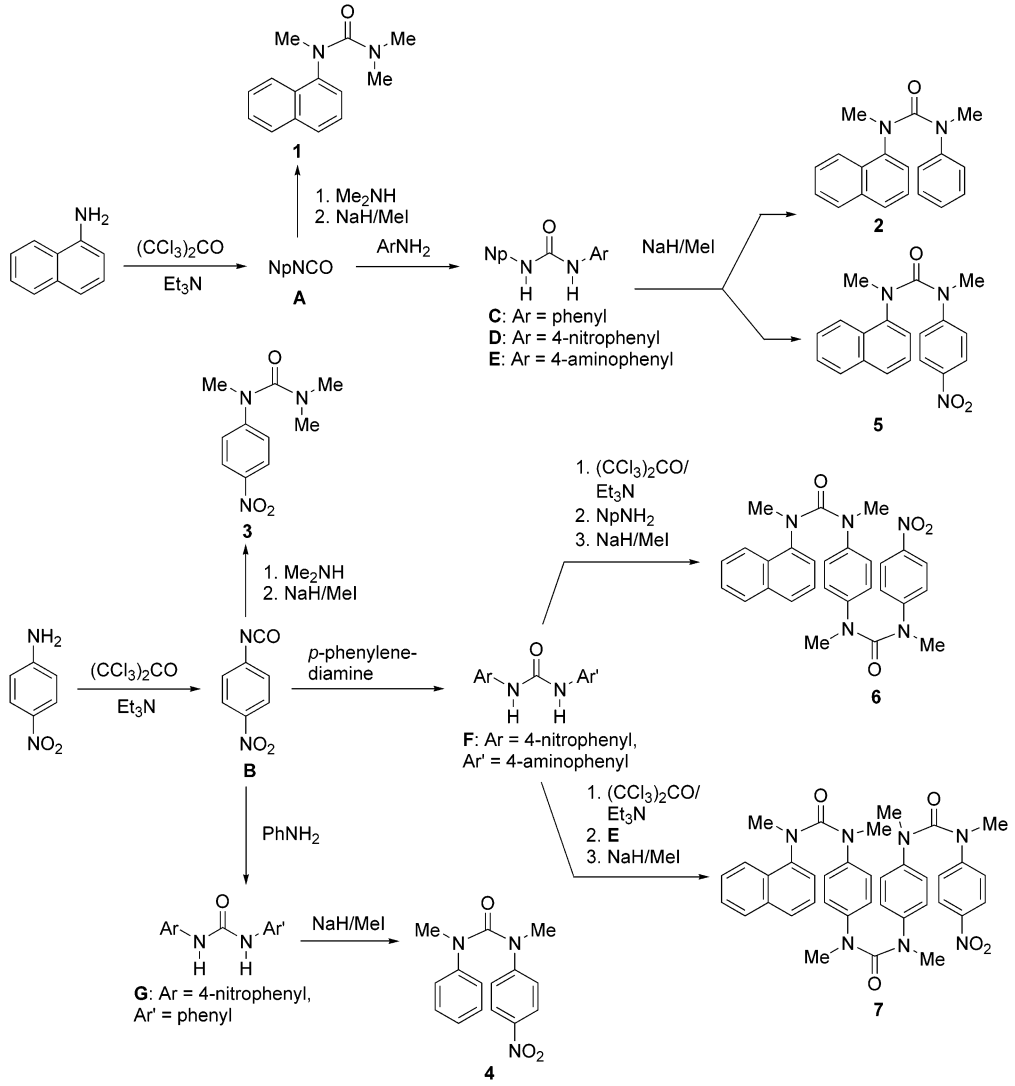
SCHEME 1. Synthesis of the Arylureas



results of our studies of the electronic interactions between aryl groups in tertiary diarylureas,[8,9] tertiary oligophenylureas,[10] and the reductive elimination of diarylureas and several oligomeric arylureas.[11] The only prior report of a donor–acceptor tertiary diaryl urea is that of Lepore et al.[12] who employed an anilsyl group as donor and nitrophenyl as acceptor. We report here the syntheses and properties of the first multilayered donor–bridge–acceptor arylureas as well as several mono- and diarylurea model compounds.

Results and Discussion

Synthesis and Structure. The synthesis of the arylureas is outlined in Scheme 1 and described in the Experimental Section and Supporting Information. The monoaryl tertiary urea **3** was prepared by the method previously described for **1**.[9] The nonsymmetrical secondary diaryl ureas **C**–**G** were prepared via the reaction of the arylisocyantates **A** and **B**, obtained by the reaction of a primary arylamine with triphosgene and triethylamine, with a second primary arylamine.[13] Yields for conversion of arylamines to isocyanates were quantitative and yields for reactions of the isocyanates with primary arylamines were typically 80%. The crude secondary diaryl ureas **C**, **D**, and **G** were methylated with sodium hydride and methyl iodide and purified by column chromatography to yield the tertiary diaryl ureas **2**, **5**, and **4**, respectively, in 50–60% yield.

A convergent strategy was employed for the synthesis of the triaryl diurea **6** and tetraaryl triurea **7**. Reaction of the isocyanates **A** and **B** with *p*-phenylenediamine afforded the secondary diarylureas **E** and **F**, respectively. Conversion of **F** to its isocyanate followed by reaction with naphthalen-1-ylamine and methylation provided **6**. Conversion of **F** to its isocyanate followed by reaction with **E** and methylation provided **7**. The yields for methylation of secondary ureas decreased from ca. 50–

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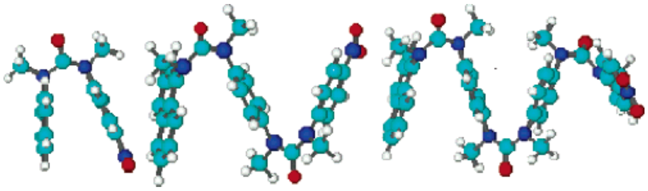

FIGURE 1. Mimimized gas-phase structures for **5**−**7**. View perpendicular to the urea plane with naphthyl on the left and nitrophenyl on the right.

TABLE 1. ^{1}H NMR Chemical Shifts of Selected Arylureas[a]

urea	naphthyl-H_2	bridging phenyl	outer phenyl
2	6.88		6.51, 6.66, 6.76
4			6.97, 7.96
5	7.01		6.76, 7.72
6	6.97	6.21, 6.32	6.82, 7.88
7	6.95	6.13, 6.24 (6.46, 6.50)[b]	6.91. 7.93

[a] Chemical shifts, ppm vs TMS in $CDCl_3$. [b] Downfield protons located on phenyl ring adjacent to nitrobenzene.

60% for the monoureas **1**−**5** to 40% for the diurea **6** and 25% for the triurea **7**, the latter reactions requiring repeated methylation cycles. The limited solubility of the secondary di- and triureas contributed to these low yields. The tertiary arylureas were characterized by their ^{1}H NMR, mass spectra, absorption spectra, and elemental analyses.

The gas-phase geometries of the arylureas **5**−**7** were optimized using the Hartree−Fock semiempirical Austin Model 1 (AM1) method,[14] which provides reliable estimated geometries for organic molecules.[15] Local minima are shown in Figure 1. The folded structure shown for **5** is ca. 3 kcal/mol more stable than the extended (unfolded) structure, as previously observed for several tertiary diarylureas.[8,9] This preference becomes larger for the di- and triureas **6** and **7** ($\Delta H°$ ~7 and 17 kcal/mol, respectively). The preference for folded structures is steric in origin, nonbonded repulsion between face-to-face phenyl rings being smaller than that between two methyl groups in extended structures. The calculated dihedral angles between the adjacent aryl rings in **2** and **5**−**7** are 41 ± 5°, and the average closest C−C contact is 3.10 ± 0.05 Å. Multiple local minima with different dihedral angles between the long-axes of adjacent phenyl rings were encountered for the folded structures, indicative of shallow ground-state potential energy surfaces.

Selected NMR data for **2** and **4**−**7** are summarized in Table 1. The naphthyl-H_2 protons appear upfield of the value for **1** (7.19 ppm). Similarly, the nitrophenyl protons of **4**−**7** are upfield of those for **3** (7.02, 8.19 ppm). Shielding of the aromatic protons is attributed to the folded geometry of the diarylureas which places the aromatic protons within the shielding region of the neighboring arene. Even greater shielding is observed for the bridging phenylene rings of **6** and **7**. In the case of **7**, the phenylene ring adjacent to naphthalene is more shielded than is the phenylene ring adjacent to nitrobenzene. The shielding in **2** is less pronounced than that for the naphthalene analogue of [2.2]paracyclophane, for which the chemical shift of the naphthyl-H_2 proton (6.62 ppm) and phenyl protons (6.33, 5.50 ppm) are further upfield.[16]

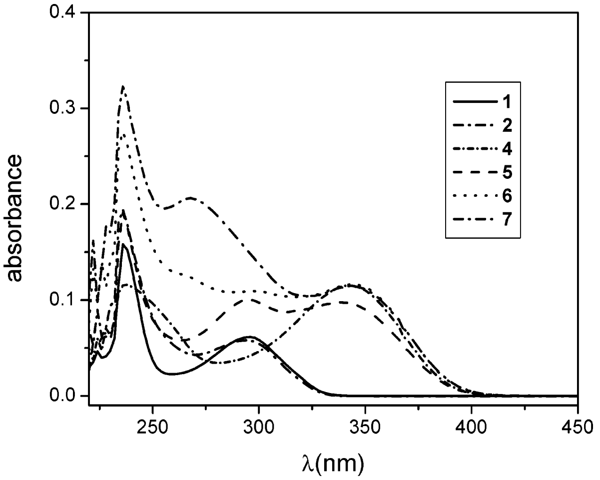

FIGURE 2. UV spectra of the arylureas (10 μM in MTHF).

TABLE 2. UV Absorption and Phosphorescence Data for Arylureas 1−7[a]

urea	λ_{abs},[b] nm	log ϵ	λ_p,[c] nm	Φ_p	τ_p, s
1	296	4.0			
2[d]	296	3.8	488	0.02	1.40
3	354	4.0			
4	342	4.1	479	0.36	0.29
5	340	4.0	488	0.18	1.38
6	342	4.1	493	0.16	1.25
7	342	4.1	492	0.18	1.32

[a] Absorption data obtained at 298 K in MTHF solution. Phosphorescence data obtained at 77 K in glassy MTHF. [b] Absorption band maximum. [c] Phosphorescence 0,0 band. [d] Fluorescence also observed at 298 K (λ_f = 407 nm, Φ_f = 0.05) and at 77 K (λ_f = 351 nm, Φ_f = 0.31).

Absorption Spectra. The ultraviolet absorption spectra of the arylureas are shown in Figure 2. The long-wavelength absorption bands of **1** and **2** are broadened and blue-shifted when compared to that for naphthalene. Their appearance is similar to that previously reported for *N,N'*-dimethyl-*N,N'*-dinaphthylurea and for the naphthalene analogue of [2.2]paracyclophane.[8,14] These bands are tentatively assigned to the overlapping naphthalene ^1L_a and ^1L_b transitions.

The absorption spectra of **3** (not shown) displays a single long-wavelength band at 352 nm (Table 2). The absorption spectrum of nitrobenzene also has a band at this position; however, it is much weaker and appears as a shoulder on a stronger band at 282 nm.[17] The two nitrobenzene long-wavelength absorption bands have been attributed to n,π* and π,π* transitions localized on the nitro group and benzene, respectively.[18,19] The 282 nm band is absent in the spectrum of **3** and also in the

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TABLE 3. Calculated Properties of Selected Singlet States[a]

urea	state	λ, nm	ϵ (L/mol/cm)	character[b]
5	S_1, S_2	449, 386	0, 3	NB, n,π*
	S_3	318	950	Np, π,π*
	S_5	310	18,600	Np → NB CT
6	S_1, S_2	449, 386	3, 3	NB, n,π*
	S_3	318	740	Np, π,π*
	S_6	304	26,400	NB π,π*
7	S_1, S_2	449, 386	11, 2	NB, n,π*
	S_3	318	1050	Np, π,π*
	S_5	305	24,880	NB π,π*

[a] Wavelength, absorbance, and character based on ZINDO calculations. Frontier orbitals and calculated spectra provided as Supporting Information. [b] NB = nitrobenzene, Np = naphthalene.

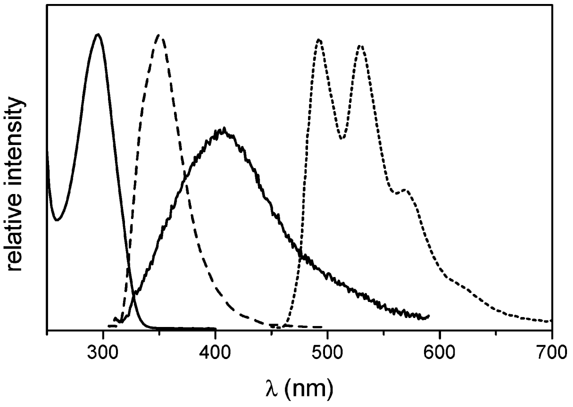

FIGURE 3. Excitation and fluorescence emission spectra of **2** at room temperature (solid lines) and fluorescence (- - -) and phosphorescence (···) at 77 K in MTHF.

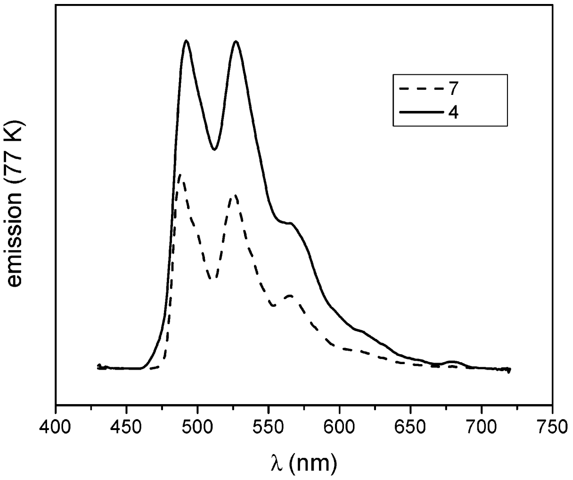

FIGURE 4. Phosporescence spectra of ureas **4** (—) and **7** (- - -) at 77 K in a MTHF glass.

spectrum of 4-nitroaniline, which has a single band at 370 nm.[20] The secondary diarylurea *N*-phenyl-*N′*-*p*-nitrophenylurea and the tertiary diarylurea *N*,*N′*-dimethyl-*N*-*p*-nitrophenyl-*N′*-anisylurea also have a single strong band near 340 nm.[12,21]

Ureas **4**−**7** have long-wavelength bands with maxima at 340−342 nm and similar molar absorbance (Table 2). Information about the origin of this band can be obtained by using the semiempirical Hartree−Fock intermediate neglect of differential overlap (INDO) method as parametrized by Zerner and co-workers (ZINDO)[22] and implemented in CAChe 6.1.10.[14] The calculated energy, absorbance, and character of selected low energy singlet states of **5**−**7** are reported in Table 3, and their calculated absorption spectra and frontier orbitals are provided in the Supporting Information. The two lowest energy transitions for **4**−**7** are assigned to a nitrobenzene-localized n,π* state with a calculated absorption maximum at 450 nm and near-zero oscillator strength. This assignment is consistent with a previous calculation for nitrobenzene using the CAS-SCF method.[19] The third transition is assigned to a naphthalene-localized π,π* state having low oscillator strength. The first allowed transition of **5** corresponds to the 5th singlet state (S_5) and is assigned to a naphthalene → nitrobenzene charge transfer state. In the case of **6** and **7** the first allowed transitions (S_6 and S_7, respectively) are assigned to nitrobenzene π,π* states.

The 290 nm bands apparent in the spectra of **5** and **6** have similar maxima and intensities to the long-wavelength bands of **1** and **2**, whereas the 260 nm bands of **6** and **7** have similar maxima to those of *N*,*N′*-dimethyl-*N*,*N′*-diphenylurea.[8] Thus, they are assigned to the π,π* transitions of the naphthyl- and phenylureas.

Emission Spectra. Urea **2** displays a broad fluorescence both at room temperature and at 77 K in MTHF and weak structured phosphorescence at 77 K (Figure 3). The room-temperature fluorescence of **2** has a mirror image relationship with the excitation spectrum, which resembles the absorption spectrum. At 77 K the fluorescence spectra of **1** and **2** are similar in energy and band shape (λ_{fl} = 355 nm). The phosphorescence spectra and decay time for **2** (Table 2) are similar to those of naphthalene (λ_p = 469 nm, τ_t = 2.3 s).[8] The temperature dependence of the spectra of **2** is similar to that for *N*,*N′*-dimethyl-*N*,*N′*-di-1-naphthylurea.[8] At room temperature, the fluorescence of **2** is red-shifted from that of **1** (407 vs 367 nm). The red-shifted fluorescence is attributed to the formation of an intramolecular exciplex between the naphthyl and phenyl rings. The absence of red-shifted fluorescence from **2** at 77 K indicates that exciplex formation does not occur in the rigid MTHF glass. Presumably the singlet state cannot undergo geometric relaxation to a more sandwich-like exciplex geometry in the MTHF glass.

The nitrophenyl ureas **3**−**7** are nonfluorescent both at room temperature and 77 K; however, they display strong, long-lived structured phosphorescence at 77 K, as shown for **4** and **7** (Figure 4 and Table 2). The absence of fluorescence both at room temperature and 77 K is consistent with a lowest energy singlet state localized on the nitrophenyl chromophore, which is known to undergo ultrafast intersystem crossing.[23] Thus, the phosphorescence of **4**−**7** may be assigned to the locally excited nitrobenzene π,π* triplet state.

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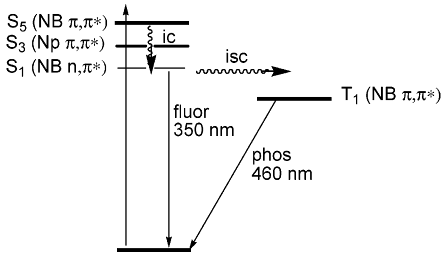
SCHEME 2. State Diagram for Ureas 6 and 7[a]



[a] NB = nitrobenzene-localized, Np = naphthalene-localized. Line widths for singlet states are proportional to transition oscillator strength (Table 3).

The information obtained from absorption spectra, ZINDO calculations, and emission spectra can be used to construct the state diagram for **6** and **7** shown in Scheme 2. Excitation of the allowed nitrobenzene π,π^* transition presumably is followed by rapid internal conversion to the dark nitrobenzene n,π^* singlet states, which undergo rapid intersystem crossing to the triplet. Rapid n,$\pi^* \rightarrow \pi,\pi^*$ intersystem crossing is consistent with El Sayed's rule.[24]

Conclusion

A convergent approach to the synthesis of nonsymmetric tertiary arylureas possessing two and three urea linkages via the exhaustive methylation of secondary ureas has been developed. Decreasing solubility of the secondary amines with added urea linkers contributes to the decreasing yields for permethylation of nitrogen. The di- and triureas **6** and **7** serve as prototypes for urea-based donor−bridge−acceptor systems in which an electron donor and acceptor are separated by a variable number of bridging phenylenediamine units.

The study of electron transfer in DBA systems requires the initial population of a locally excited-state acceptor (DBA*) or donor (D*BA) followed by formation of a charge transfer state ($D^{+\bullet}BA^{-\bullet}$). The combination of naphthyl donor and nitrobenzene acceptor is not suitable for electron transfer or energy transfer studies because of localization of both the lowest singlet and triplet excitation on the nitrobenzene chromophore. Thus the investigation of electron-transfer dynamics in tertiary-urea based DBA systems will require the deployment of alternative donor and acceptor groups.

Experimental Section

The synthesis of 1,1,3-trimethyl-3-naphthalen-1-ylurea (**1**) has been previously described.[9] The synthesis of secondary unsymmetrical diarylureas follows the method of Majer and Randad.[13]

1,3-Dimethyl-1-naphthalen-1-yl-3-phenylurea (2). To a solution of triphosgene (10 mmol) in DCM (20 mL) was added dropwise naphthalen-1-ylamine (10 mmol) in DCM (20 mL) followed by the dropwise addition of triethylamine (3 mL) in DCM (10 mL). The solvent was removed on a rotary evaporator. The resulting residue was dissolved in DCM (20 mL), and aniline (10 mmol) in DCM (20 mL) was added. After the mixture was refluxed for 30 min, the solvent was removed on a rotary evaporator. The residue was dissolved in acetone (30 mL) and mixed with water (30 mL). The precipitate was collected on a funnel by vacuum filtration and washed with water−acetone (1:1, 4 × 5 mL) to afford **C** (70% yield, 1.8 g, >95% purity by ^{1}H NMR in DMSO-d_6) as a white solid: MS *m/z* 263 ($M^{+\bullet}$). NaH (20 mmol) was washed with hexanes (3 × 5 mL) and dissolved in dry DMF (30 mL). The solution was added dropwise in 6 portions over 30 min into a solution of **C** (5 mmol) in DMF (20 mL). Following each portion of NaH in DMF was the dropwise addition of CH_3I (20 mmol, 6 × 0.2 mL). The resulting mixture was stirred for an additional 2 h, at which time all starting material was consumed (as monitored by TLC). DCM (40 mL) was added to the mixture, and the resulting organic layer was washed with water (3 × 50 mL) and then dried over K_2CO_3 (5 g). The solvent was removed on a rotary evaporator, and the resulting residue was chromatographed on silica gel using hexanes−acetone (2:1) as eluent to give a white solid **2** (60%, 0.9 g): mp 51−53 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.12 (s, 3H), 3.31 (s, 3H), 6.51 (d, J = 7.5, 2H), 6.66 (d, J = 7.5, 1H), 6.76 (dd, J = 7.5, J = 7.5, 2H), 6.88 (d, J = 7.5, 1H), 7.12 (dd, J = 7.5, J = 7.5, 1H), 7.38 (m, 2H), 7.51 (d, J = 8.0, 1H), 7.68 (m, 2H); MS *m/z* calcd for $C_{19}H_{18}N_2O$ 290.4, found 291.4. Anal. Calcd for $C_{19}H_{18}N_2O$: C, 78.59; H, 6.25; N, 9.60, Found: C, 78.35; H, 6.27; N, 9.67.

1,1,3-Trimethyl-3-(4-nitrophenyl)urea (3) was prepared by the method previously described for **1**:[9] mp 70−72 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.86 (s, 6H), 3.30 (s, 3H), 7.02 (d, J = 9.0, 2H), 8.19 (d, J = 9.0, 2H); MS *m/z* calcd for $C_{10}H_{13}N_3O_3$ 223.2, found 224.3.

1,3-Dimethyl-1-(4-nitrophenyl)-3-phenylurea (4). To a solution of triphosgene (10 mmol) in DCM (20 mL) was added dropwise *p*-nitroaniline (10 mmol) in DCM (20 mL) followed by the dropwise addition of triethylamine (2.8 mL) in DCM (10 mL). The mixture was stirred for 30 min. The solvent was removed on a rotary evaporator. The resulting residue was dissolved in DCM (20 mL), and aniline (10 mmol) in DCM (20 mL) was added. After the mixture was refluxed for 30 min, the solvent was removed on a rotary evaporator. The residue was dissolved in acetone (20 mL) and mixed with water (10 mL). The precipitate was collected on a funnel by vacuum filtration and washed with water (3 × 10 mL) and then water−acetone (1:1, 2 × 5 mL) to afford **G** (80%, 2.0 g, >95% purity by ^{1}H NMR in DMSO-d_6) as a yellow solid. NaH (20 mmol) was washed with hexanes (3 × 5 mL) and dissolved in dry DMF (20 mL). The solution was added dropwise in 6 portions over 30 min into a solution of **G** (5 mmol) in DMF (10 mL). Following each portion of NaH in DMF was the dropwise addition of CH_3I (20 mmol, 6 × 0.2 mL). The resulting mixture was stirred for an additional 2 h, at which time all starting material was consumed (as monitored by TLC). DCM (40 mL) was added to the mixture, and the resulting organic layer was washed with water (3 × 40 mL) and then dried over K_2CO_3 (5 g). The solvent was removed on a rotary evaporator, and the resulting residue was chromatographed on silica gel using hexanes−acetone (2:1) as eluent to give a yellow liquid. The liquid was rechromatographed on silica gel using hexanes−acetone (2:1) as eluent to give a crystalline solid **4** (21%, 0.3 g): mp 144−146 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.19 (s, 3H), 3.32 (s, 3H), 6.88 (d, J = 6.0, 2H), 6.97 (d, J = 7.2, 2H), 7.01 (dd, J = 6.0, J = 6.0, 1H), 7.12 (dd, J = 6.0, J = 6.0, 2H), 7.96 (d, J = 7.2, 2H); MS *m/z* calcd for $C_{15}H_{15}N_3O_3$ 285.3, found 286.3.

1,3-Dimethyl-1-naphthalen-1-yl-3-(4-nitrophenyl)-urea (5). To a solution of triphosgene (10 mmol) in DCM (10 mL) was added dropwise *p*-nitroaniline (10 mmol) in DCM (20 mL) followed by the dropwise addition of triethylamine (1.4 mL) in DCM (10 mL). The mixture was stirred for 15 min. The solvent was removed on a rotary evaporator. The resulting residue was dissolved in DCM (20 mL), and naphthalen-1-ylamine (10 mmol) in DCM (10 mL) was added along with triethylamine (1.4 mL). After the mixture was refluxed for 30 min, the solvent was removed on a rotary evaporator. The residue was kept at 100 °C for 30 min then dissolved in acetone (20 mL) and mixed with water (20 mL). The precipitate was

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collected on a funnel by vacuum filtration and washed with water (3 × 20 mL) and then recrystallized with DMF−water (10:1) to afford **D** (80%, 2.5 g, ca. 80% purity by ^{1}H NMR in DMSO-d_6) as a yellow solid. NaH (10 mmol) was washed with hexanes (3 × 5 mL) and dissolved in dry DMF (10 mL). The solution was added dropwise in 3 portions over 30 min into a solution of **D** (3 mmol) in DMF (20 mL). Following each portion of NaH in DMF was the dropwise addition of CH_3I (10 mmol, 3 × 185 μL). The resulting mixture was stirred for an additional 3 h, at which time all starting material was consumed (as monitored by TLC). Ethyl acetate (50 mL) was added to the mixture, and the resulting organic layer was washed with water (3 × 30 mL) and then dried over K_2CO_3 (3 g). The solvent was removed on a rotary evaporator, and the resulting residue was recrystallized with ethyl acetate−hexanes (1:1). The crude product was chromatographed on silica gel using ethyl acetate−hexanes (10:1) as eluent to give a yellow crystalline solid **5** (50%, 0.5 g): mp 138−140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.14 (s, 3H), 3.21 (s, 3H), 6.76 (d, J = 7.2, 2H), 7.01 (d, J = 6.0, 1H), 7.22 (dd, J = 6.0, J = 6.4, 1H), 7.45 (dd, J = 5.6, J = 6.0, 1H), 7.50 (dd, J = 6.0, J = 6.0, 1H), 7.61 (d, J = 6.8, 1H), 7.73 (m, 4H); MS m/z calcd for $C_{19}H_{17}N_3O_3$ 335.4, found 336.3. Anal. Calcd for $C_{19}H_{17}N_3O_3$: C, 68.05; H, 5.11; N, 12.53. Found C, 68.07; H, 5.09; N, 12.47.

1-[4-(1,3-Dimethyl-3-naphthalen-1-yl-ureido)phenyl]-1,3-dimethyl-3-(4-nitrophenyl)urea (6). To a solution of triphosgene (20 mmol) in DCM (20 mL) was added dropwise *p*-nitroaniline (10 mmol) in DCM (100 mL) over 10 min followed by the dropwise addition of triethylamine (6.0 mL) in DCM (20 mL) over 10 min. The mixture was stirred for 20 min. The solution was added dropwise into a refluxing solution of *p*-phenylenediamine (80 mmol) in DCM (40 mL). After the mixture was refluxed for 10 min, the solvent was removed on a rotary evaporator. The residue was dissolved in acetone (30 mL) and mixed with water (50 mL). The precipitate was collected on a funnel by vacuum filtration and washed with water (50 mL) to afford **F** (87%, 4.6 g, ca. 85% purity by ^{1}H NMR in DMSO-d_6) as an orange solid: MS m/z 272 ($M^{+\bullet}$). To a solution of triphosgene (3 mmol) in DCM (10 mL) was added dropwise **F** (3 mmol) in DCM (50 mL) followed by the dropwise addition of triethylamine (0.9 mL) in DCM (5 mL). The mixture was stirred for 10 min. The precipitate was filtered on a funnel by vacuum filtration and the filtrate was collected. The solvent was removed on a rotary evaporator. The resulting residue was dissolved in DCM (20 mL) and added dropwise to a solution of naphthalen-1-ylamine (3 mmol) in DCM (10 mL). After refluxing for 10 min, the solvent was removed on a rotary evaporator. The residue was combined with acetone (10 mL). The precipitate was collected on a funnel by vacuum filtration and washed with water (3 × 10 mL) and then acetone (10 mL) to afford the diurea (65%, 0.8 g, ca. 90% purity by ^{1}H NMR in DMSO-d_6) as a yellow solid: MS m/z 441 ($M^{+\bullet}$). NaH (30 mmol) was washed with hexanes (3 × 5 mL) and dissolved in dry DMF (20 mL). The solution was added dropwise in 9 portions over 30 min into a solution of the diurea (1.5 mmol) in DMF (30 mL). Following each portion of NaH in DMF was the dropwise addition of CH_3I (30 mmol, 9 × 0.2 mL). The resulting mixture was stirred for an additional 2 h, at which time all starting material was consumed (as monitored by TLC). DCM (50 mL) was added to the mixture, and the resulting organic layer was washed with water (3 × 30 mL) and then dried over K_2CO_3 (5 g). The solvent was removed on a rotary evaporator, and the resulting residue was chromatographed on silica gel using hexanes−acetone (3:1) as eluent to give a yellow powder. The solid was recrystallized with DCM−hexanes (1:1) to give a yellow crystalline solid **6** (33%, 0.25 g): mp 193−195 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.86 (s, 3H), 2.96 (s, 3H), 3.01 (s, 3H), 3.24 (s, 3H), 6.22 (d, J = 8.0, 2H), 6.32 (d, J = 8.0, 2H), 6.82 (d, J = 9.2, 2H), 6.97 (dd, J = 7.2, J = 7.2, 1H), 7.18 (dd, J = 8.0, J = 8.0, 1H), 7.30−7.37 (m, 2H), 7.50 (d, J = 8.4, 1H), 7.56 (d, J = 8.0, 1H), 7.65 (d, J = 9.2, 1H), 7.88 (d, J = 9.2, 2H); MS m/z 497 ($M^{+\bullet}$). Anal. Calcd for $C_{28}H_{27}N_5O_4$: C, 67.59; H, 5.47; N, 14.08. Found C, 67.38; H, 5.51; N, 14.14.

Urea 7. To a solution of triphosgene (20 mmol) in DCM (20 mL) was added dropwise naphthalen-1-ylamine (20 mmol) in DCM (50 mL) over 10 min followed by the dropwise addition of triethylamine (6.0 mL) in DCM (20 mL). The mixture was stirred for 20 min. The solution was added dropwise into a refluxing solution of *p*-phenylenediamine (80 mmol) in DCM (50 mL). After the mixture was refluxed for 10 min, the solvent was removed on a rotary evaporator. The residue was mixed with acetone (30 mL) and water (30 mL). The precipitate was collected on a funnel by vacuum filtration and washed with acetone−water (1:1, 3 × 10 mL) to afford **E** (80%, 4.5 g, 90% purity by ^{1}H NMR in DMSO-d_6) as a gray powder. To a solution of triphosgene (2.5 mmol) in DCM (10 mL) was added dropwise **F** (7.5 mmol) in DCM (50 mL) followed by the dropwise addition of triethylamine (2.8 mL) in DCM (10 mL). The mixture was stirred for 10 min. The resulting solution was added dropwise into a refluxing suspension of **E** (7.5 mmol) in DCM (30 mL). After refluxing for 30 min, the solvent was removed on a rotary evaporator. The residue was combined with acetone (30 mL) and water (30 mL). The precipitate was collected on a funnel by vacuum filtration and washed with acetone (3 × 10 mL), water (2 × 10 mL), and acetone (2 × 10 mL) to afford the triurea (70%, 2.8 g, ca. 85% purity by ^{1}H NMR in DMSO-d_6) as a brown solid. NaH (50 mmol) was washed with hexanes (3 × 10 mL) and dissolved in dry DMF (30 mL). The solution was added dropwise in 30 portions over 60 min into a solution of the triurea (3 mmol) in DMF (30 mL). Following each portion of NaH in DMF was the dropwise addition of CH_3I (50 mmol, 30 × 0.1 mL). The resulting mixture was stirred for an additional 1 h, at which time all starting material was consumed (as monitored by TLC). DCM (50 mL) was added to the mixture, and the resulting organic layer was washed with water (3 × 30 mL) and then dried over K_2CO_3 (5 g). The solvent was removed on a rotary evaporator, and the resulting residue was chromatographed on silica gel using hexanes−acetone (1:1, 1% triethylamine) as eluent to give a yellow powder. The solid was recrystallized with DCM−acetone−hexanes (1:1:1) to give a yellow crystalline solid **7** (10%, 0.2 g): mp 213-215 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.71 (s, 3H), 2.86 (s, 3H), 3.02 (s, 3H), 3.09 (s, 3H), 3.13 (s, 3H), 3.25 (s, 3H), 6.13 (bs, 2H), 6.24 (bs, 2H), 6.46 (bs, 2H), 6.50 (bs, 2H), 6.90 (d, J = 7.4, 2H), 6.95 (bs, 2H), 7.16 (bs, 2H), 7.32 (bs, 2H), 7.49 (d, J = 8.0, 1H), 7.55 (bs, 2H), 7.63 (d, J = 8.4, 1H), 7.93 (d, J = 7.4, 2H); MS m/z 655 ($M^{+\bullet}$). Anal. Calcd for $C_{37}H_{37}N_{75}O_5$: C, 67.36; H, 5.65; N, 14.86. Found: C, 67.30; H, 5.73; N, 14.86.

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Supporting Information Available: General methods and materials; ^{1}H NMR spectra of ureas **3** and **4**; ZINDO calculated frontier orbitals and spectra and Cartesian coordinates and total energies of ureas **5**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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