

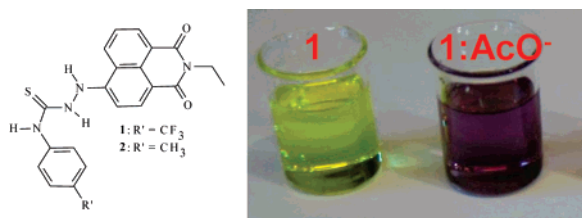
Colorimetric “Naked Eye” Sensing of Anions in Aqueous Solution

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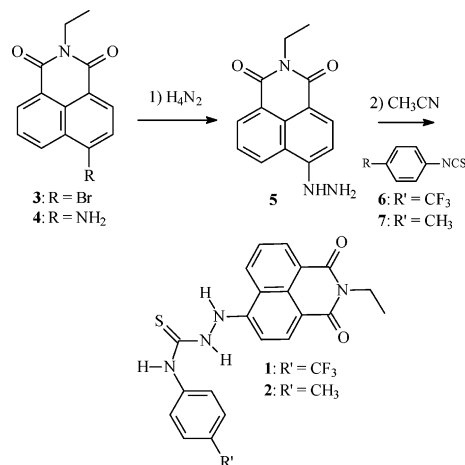
Received September 29, 2005



The synthesis and UV–vis and NMR spectroscopic studies of thiourea-based colorimetric sensors for anions are presented. These sensors can recognize anions through hydrogen bonding even in competitive pH-buffered aqueous solutions, giving rise to large color changes that are clearly visible to the naked eye.

Luminescent and colorimetric anion recognition and sensing is a rapidly developing field within supramolecular chemistry.¹ As inspiration, nature provides us with many great examples of anion recognition motifs, primarily based on hydrogen-bonding interactions at charged or charge-neutral organic receptors.² Employing these inherently weak interactions as the foundation of receptor design to mimic these recognition events is notoriously difficult as solvent molecules compete more effectively for both the receptor (host) and anion (guest). However, we recently demonstrated the first examples of anion sensing using charge-neutral thiourea hydrogen-bonding motifs in fluorescent PET chemosensors.³ De-

SCHEME 1. Synthesis of Sensors 1 and 2



spite our success, anion sensing *only* ever occurred in noncompetitive organic solvents. This shortcoming is also prevalent in many examples throughout the literature.^{1,4,5} Clearly there is a need to develop receptors capable of anion binding within competitive media to more accurately mimic those interactions found in nature. In this note, we present two naphthalimide-based receptors, **1** and **2**, which belong to a family of new charge-neutral colorimetric internal charge transfer (ICT) chemosensors.⁶ The recognition of the biologically important AcO^- , H_2PO_4^- , and F^- anions is achieved in aqueous solution via hydrogen bonding at charge-neutral sites. Furthermore, the anion binding is accompanied by a visually striking color change, giving naked eye anion sensing.

Sensors **1** and **2** were made (Scheme 1) by first reacting *N*-ethyl-4-bromo-1,8-naphthalimide (**3**)⁷ with hydrazine monohydrate to give **5** as a yellow solid in 93% yield. Reaction of **5** with either 4-(trifluoromethyl)phenyl- (**6**) or 4-(methyl)phenyl- (**7**) isothiocyanates gave **1** and **2**, respectively. Single crystals of **1** suitable for an X-ray diffraction study were grown from EtOH. The structure of **1** revealed the thiourea protons to be in the anti-conformation and that adjacent molecules participate in numerous intermolecular interactions. The combination

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(6) Recent excellent examples include: (a) Thiagarajan, V.; Ramamurthy, P.; Thirumalai, D.; Ramakrishnan, T. *Org. Lett.* **2005**, *7*, 657. (b) Esteban-Gómez, D.; Fabbri, L.; Licchelli, M.; Esteban-Gómez, D. *J. Org. Chem.* **2005**, *70*, 5717. (c) Fabbri, L.; Licchelli, M.; Monzani, E. *Org. Biomol. Chem.* **2005**, *3*, 1495. (d) Liu, B.; Tian, H. *Chem. Lett.* **2005**, *34*, 686. (e) Jose, D. A.; Kumar, D. K.; Ganguly, B.; Das, A. *Org. Lett.* **2004**, *6*, 3445. (f) Vázquez, M.; Fabbri, L.; Taglietti, A.; Pedrido, R. M.; González-Noya, A. M.; Bermejo, M. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 1962. (g) Camiolo, S.; Gale, P. A.; Hursthouse, M. B.; Light, M. E. *Org. Biomol. Chem.* **2003**, *1*, 741. (h) Jiménez, D.; Martínez-Mañez, R.; Sancenón, F.; Soto, J. *Tetrahedron Lett.* **2002**, *43*, 2823. (i) Miyaji, H.; Sessler, J. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 154. (j) Lee, D. H.; Lee, K. H.; Hong, J. I. *Org. Lett.* **2001**, *3*, 5. (k) Niikura, K.; Bisson, A. P.; Slyn, E. V. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1111.

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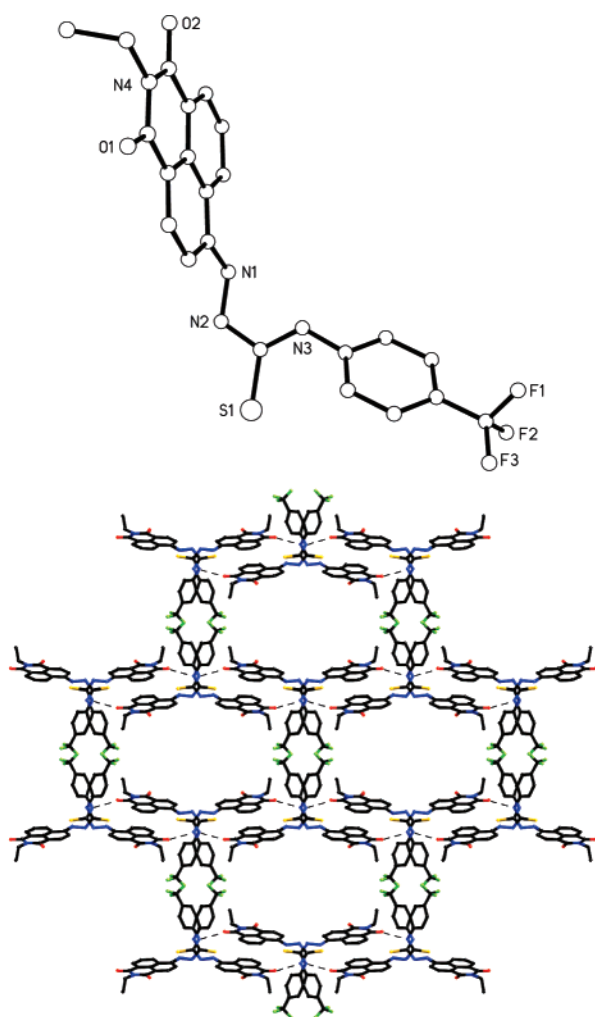


FIGURE 1. Structure of **1** showing the *anti* conformation of the thiourea moiety (top) and the 3-D network it forms (bottom). H atoms and solvent molecules omitted for clarity.

of H-bonding, face-to-face π - π stacking, and short F \cdots F contacts⁸ give rise to an elaborate 3D network that is perforated with solvent-filled channels (Figures 1 and S1). Poorer quality crystals of **2** may also be isolated from EtOH.⁹

The spectroscopic investigation of **1** and **2** was first carried out in DMSO. Sensor **1** (1×10^{-4} M) showed a broad absorption band centered at 414 nm and a smaller shoulder at 560 nm.¹⁰ Upon addition of anions such as AcO⁻, H₂PO₄⁻, and F⁻ (as their tetrabutylammonium salts), the band at 560 nm increased in intensity at the expense of the 414-nm transition. Furthermore, a new band at 350 nm and two clear isosbestic points were

observed at 465 and 380 nm, respectively (Figure S2). The yellow to deep purple color change is clearly evident to the naked eye (Figure S3). We propose that these changes are consistent with the anions binding to the thiourea moiety through hydrogen bonding. For such recognition to occur, the thiourea protons need to be in *syn* orientation. It is also possible that the proton of the 4-amino moiety is aiding in the binding of the anion and that these combined binding modes give rise to enhanced ICT character with concomitant color changes. This hypothesis is further supported by the fact that the absorption spectrum of **4** has a λ_{max} at ca. 460 nm, which suggests that the lone pair of the 4-amino moiety of **1** is not fully engaged in the ICT prior to the binding.¹¹

By observing the changes in the 560-nm band of **1** as a function of increasing concentration of AcO⁻ (as $-\log[\text{AcO}^-]$), a sigmoidal curve was observed that changed over two log units. This is characteristic of 1:1 binding and simple equilibrium (Figure S2b).^{3,12} Nonlinear least-squares regression analysis of these changes gave a binding constant $\log \beta = 4.95 (\pm 0.1)$. When these measurements were repeated using **5**, no such changes occurred (e.g. the thiourea functional group is essential to successful anion sensing and consequent color changes). Similarly, titration with F⁻ or H₂PO₄⁻ gave rise to comparable spectral changes with binding constants of 4.4 (± 0.1) (Figure S4) and 4.0 (± 0.1), respectively. No significant changes were observed using other halides (e.g. Cl⁻ or Br⁻). However, it is worth noting that at higher F⁻ concentrations there were distinctive changes in the absorption spectra that we assign to the deprotonation of the 4-aminonaphthalimide moiety and the formation of bifluoride (HF₂⁻) (Figure S3, see later discussion).^{7,13} Similar results were observed for **2**, with a $\log \beta$ of 4.3 (± 0.1) for F⁻, demonstrating that the nature of the aromatic moiety of the receptor (CF₃ versus CH₃) does not greatly alter the binding affinity. This is possibly due to the “overriding effect” of the ICT nature of the naphthalimide unit over the phenyl.

The binding of anions was also clear from ¹H NMR spectroscopy (DMSO-*d*₆) by monitoring the thiourea protons of **2** that initially appear at 10.04 and 10.06 ppm and the aromatic N-H proton at 9.86 ppm (Figure S5). This revealed that the binding of anions resulted in slow exchange of the protons as titration with either F⁻ or AcO⁻ showed the formation of two new thiourea proton resonances at 8.05 and 11.2 ppm (Figure 2). For AcO⁻ the aromatic N-H was also visible as a broad signal appearing at ca. 12 ppm, but after ca. 0.8 equiv of AcO⁻

(11) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515.

(12) This binding was also visible in the fluorescence emission spectra. When exciting at 404 nm, a broad emission band centered at ca. 440 nm was observed that reduced in intensity upon addition of anions with the formation of two bands at 510 and 635 nm, respectively. We do not believe that we have a large contribution of aggregation in the sample as the NMR did not change upon dilutions. However, we cannot disregard the fact that urea and thiourea compounds are known to aggregate to a degree and hence that the anion addition might affect the nature of this aggregation if present. Nevertheless, the fact that Cl⁻ and Br⁻ did not give rise to any spectral changes strongly supports our explanation. Unfortunately, as **1** and **2** are insoluble in neat H₂O it was not possible to carry out an identical investigation in this solvent.

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(9) The packing of **1** suggests that the CF₃ groups self-aggregate and play a significant structure-directing role that allows the growth of good quality crystals (cf. **2**) and propagates the formation of channels via short F \cdots F contacts.⁸ These channels account for a staggering 36% of the crystal volume, attesting to the strength of these multiple interactions.

(10) The ratio between these two bands was highly concentration-dependent, whereas at low concentration the 560-nm band was substantially more intense than at higher concentrations (see Supporting Information). Quartz cells and glassware were used in all of these measurements.

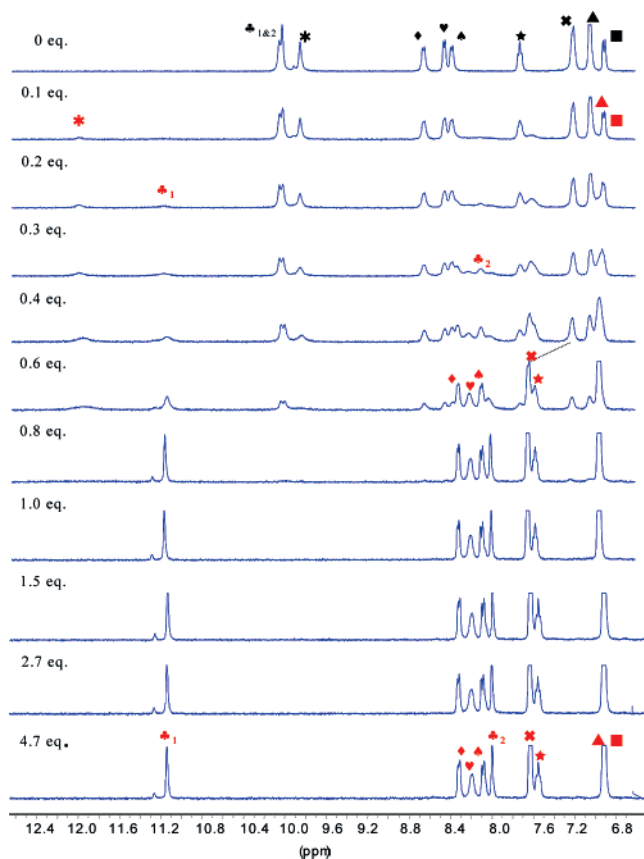


FIGURE 2. Stack plot of ^1H NMRs of **2** on addition of AcO^- ($\text{DMSO}-d_6$, 400 MHz). Black symbols show position of resonance before addition of anion, and red symbols show position of resonance upon binding.

it had broadened and disappeared. Integration of these newly formed signals confirmed the 1:1 binding seen in the absorption spectra. For AcO^- (Figures 2 and S6), no further changes occurred after the addition of 1 equiv. However, excess F^- (1 \rightarrow 5.2 equiv) caused further changes, with the appearance of a new signal at 16.1 ppm after ca. 3 equiv with significant changes in all the resonances supporting the formation of HF_2^- (Figures 3 and S7).^{7,13}

The most important result from our current study is that, upon addition of competitive hydrogen-bonding solvents such as ethanol or water, the color changes were *not* reversed.^{4,5} We thus carried out identical titrations of **1** in EtOH, where **1** showed a strong absorption band at 404 nm and a smaller shoulder at 540 nm. The titration of this solution with AcO^- (Figure S8), F^- , or H_2PO_4^- gave rise to distinctive color changes. For AcO^- , a new band at 340 nm and isosbestic points at 368 and 454 nm were observed. For the changes in the 540 nm band, $\log \beta$ values of 4.47 (± 0.1), 3.80 (± 0.1), and 3.48 (± 0.1) were determined for these anions, respectively. No such changes were seen for **5** (*which lacks the thiourea part*) upon addition of AcO^- under identical conditions. Similar compounds functionalized with alkyl changed at this amino moiety have also been prepared in our previous work,⁷ and these also showed no binding toward AcO^- . This clearly demonstrates that **1** is capable of sensing anions in highly competitive media, where the recognition is through hydrogen bonding. Furthermore,

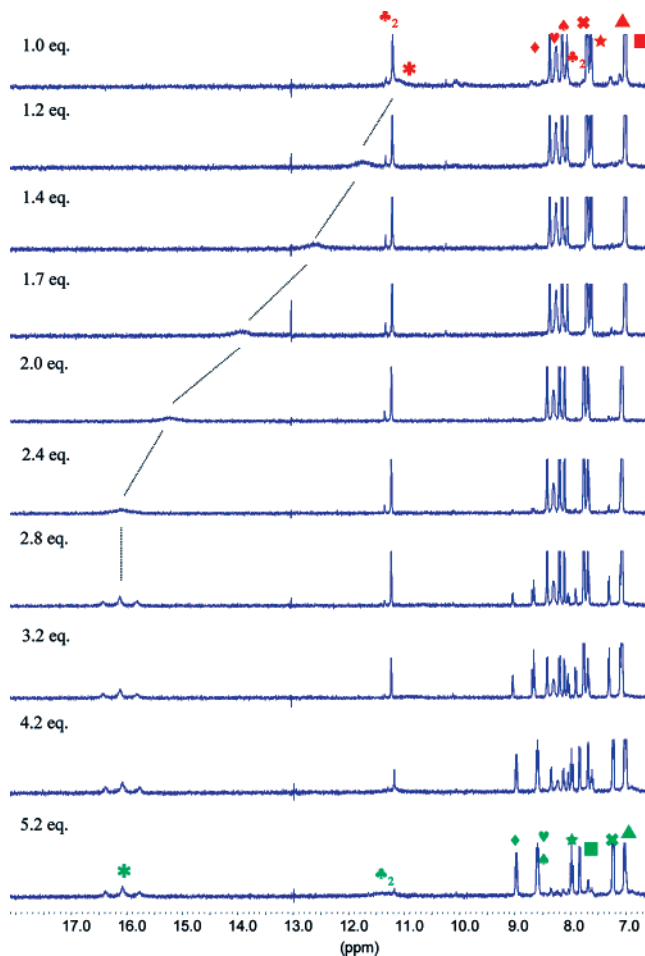


FIGURE 3. Stack plot of ^1H NMRs of **2** with F^- (1–5.2 equiv, $\text{DMSO}-d_6$, 400 MHz). The dashed line tracks the formation of HF_2^- .

the addition of excess F^- did *not* give rise to the changes in the absorption spectra as seen previously, suggesting that no deprotonation of the naphthalimide amine or the thiourea had occurred. Encouraged by these remarkable results, we undertook the same titrations in 1:1 EtOH/ H_2O mixture. Under these conditions, two bands were seen in the absorption spectra at 407 nm (major band) and 548 nm (minor band) for **1**. Upon titration with AcO^- (Figure 4; see also Figure S9), similar effects were observed as seen previously in DMSO and EtOH solutions. As before, the changes were clearly visible to the naked eye and occurred over two log units (Figure 4 inset), giving $\log \beta$ values of 3.4 (± 0.1), 2.2 (± 0.1), and ~ 1 (± 0.2) for AcO^- , F^- , and H_2PO_4^- , respectively. We also evaluated the response of **1** to a series of anions using their corresponding sodium salts. Of these, ClO_4^- , SO_4^{2-} , and Br^- were not detected, whereas NaF produced results identical to that seen for TBAF. With the aim of excluding the possibility of these changes being due to pH changes, we carried out the same experiments in 1:1 EtOH/ H_2O imidazole/HBr (10 mM) buffered solution at pH 7.15 for **1** and at pH 7.3 for **2**.¹⁴ Once more, similar color changes were observed as above (cf. Figures S10 and S11 for AcO^- and H_2PO_4^- , respectively). It should also be noted that the pH of the solution *did not* change by more than 0.15 units during these titrations, clearly excluding any pH

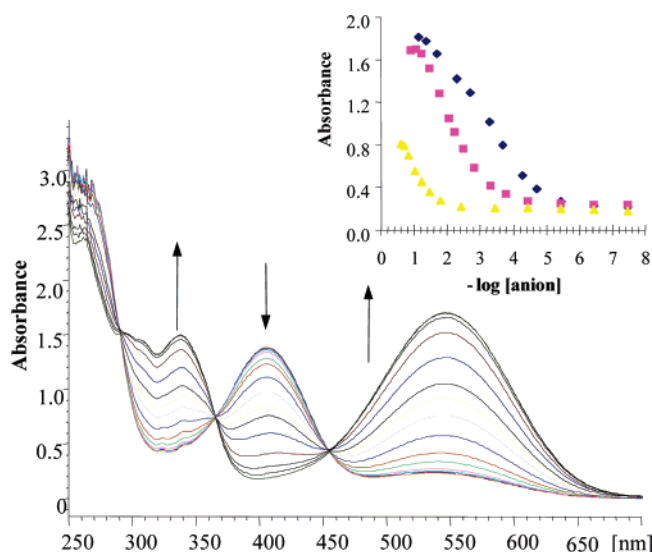


FIGURE 4. Changes in the absorption spectra of **1** on addition of F^- in 1:1 EtOH/ H_2O solution. Inset shows the changes at 548 nm as a function of $-\log[\text{anion}]$: $\blacklozenge = \text{AcO}^-$, $\blacksquare = F^-$, and $\blacktriangle = \text{H}_2\text{PO}_4^-$.

effects. To the best of our knowledge, these are the first examples of colorimetric (and luminescence) anion sensors that can be used in highly competitive aqueous media where the recognition event is mediated through bonding to a charge-neutral receptor that causes concomitant changes in the ICT character of the sensors.¹⁵

In summary, we have developed novel colorimetric anion sensors for use in aqueous solution where anion sensing occurs with concomitant yellow to purple color changes. We are currently investigating these unique features in greater detail.

Experimental Section

6-Bromo-2-ethylbenzo[de]isoquinoline-1,3-dione (3). 4-Bromo-1,8-naphthalic anhydride (2.00 g, 7.2 mmol) and ethylamine (70% soln in water) (0.69 mL, 8.66 mmol) were refluxed in 1,4-dioxane (100 mL) for 7 h. The solution was then poured into water to precipitate out a solid, which was collected by filtration, washed with water, and dried to yield **3** as a cream-colored solid (1.96 g, 89%). mp 160–162 °C (lit. mp 163 °C); Anal. Calcd for $\text{C}_{14}\text{H}_{10}\text{BrNO}_2$: C 55.29, H 3.31, N 4.61. Found: C 55.22, H 3.32, N 4.73; δ_{H} (400 MHz, CDCl_3): 1.34 (3H, t, $J = 7.0$ Hz, CH_3), 4.24 (2H, q, $J = 7.0$ Hz, CH_2), 7.82 (1H, dd, $J = 7.8$ and 8.0 Hz, Ar–H), 8.00 (1H, d, $J = 8.0$ Hz, Ar–H), 8.38 (1H, d, $J = 8.0$ Hz, Ar–H), 8.51 (1H, d, $J = 8.5$ Hz, Ar–H), 8.62 (1H, d, $J = 7.5$ Hz, Ar–H); δ_{C} (400 MHz, CDCl_3): 12.8, 35.2, 121.9, 122.7, 127.5, 128.5, 129.6, 130.1, 130.5, 130.6, 131.4, 132.6, 162.8, 162.9.

(14) Spectroscopic pH titrations of **1** and **2** showed that the color changes similar to those seen above only occurred in alkaline pH. See Figures S12 and S13 for **1** and **2**, respectively. These changes were fully reversible. Also note that the changes occurring in Figure 3 all took place in a pH window well below that seen in Figures S12 and S13.

(15) Anion sensing has been demonstrated at a 1,3-dichloroethane–water interface: Kato, R.; Cui, Y.-Y.; Nishizawa, S.; Yokobori, T.; Teramae, N. *Tetrahedron Lett.* **2004**, *45*, 4273 and references therein.

2-Ethyl-6-hydrazinobenzo[de]isoquinoline-1,3-dione (5). Hydrazine monohydrate (excess) was added to **3** (0.20 g, 0.66 mmol). This reaction mixture was heated at 130 °C and left stirring for 1 h. The mixture was then poured into water to precipitate out a solid, which was collected by filtration, washed with water, and dried to yield **5** as a yellow solid (0.16 g, 93%). mp 255–257 °C; HRMS: Calcd for $\text{C}_{14}\text{H}_{14}\text{N}_3\text{O}_2$ [$M + H$]⁺ 256.1086, found 256.1077; δ_{H} (400 MHz, $(\text{CD}_3)_2\text{SO}$): 1.18 (3H, t, $J = 7.0$ Hz, CH_3), 4.05 (2H, q, $J = 7.0$ Hz, CH_2), 4.69 (2H, d, $J = 10.6$ Hz, NH_2), 7.24 (1H, d, $J = 8.6$ Hz, Ar–H), 7.64 (1H, dd, $J = 7.8$ and 8.0 Hz, Ar–H), 8.28 (1H, d, $J = 7.5$ Hz, Ar–H), 8.41 (1H, d, $J = 7.0$ Hz, Ar–H), 8.61 (1H, d, $J = 8.5$ Hz, Ar–H), 9.13 (1H, br, NH); δ_{C} (100 MHz, $(\text{CD}_3)_2\text{SO}$): 13.3, 34.2, 104.0, 107.4, 118.4, 121.7, 124.1, 127.3, 128.2, 130.5, 134.2, 153.2, 162.7, 163.6; m/z 256 ($M + H$)⁺; $\nu_{\text{max}}/\text{cm}^{-1}$ 3450, 3366, 3316, 1672, 1636, 1614, 1578, 1540, 1439, 1389, 1366, 1346, 1310, 1251, 114, 1069, 950, 772.

General Synthesis of Thioureas. The relevant amine and isothiocyanate (1.1 equiv) were refluxed for 3 days in CH_3CN . The solution was then washed with 0.5 M HCl and water. The organic layer was dried over MgSO_4 , filtered, and evaporated to dryness. Purification of the crude product was carried out by trituration with chloroform.

6-[1-Amino-3-(4-trifluoromethylphenyl)-thiourea]-2-ethylbenzo[de]isoquinoline-1,3-dione (1). **1** was synthesized according to the above procedure, using **5** (0.20 g, 0.73 mmol) and 4-(trifluoromethyl)phenyl isothiocyanate (0.15 g, 0.73 mmol), yielding the desired product as a brown solid (0.05 g, 15%). mp 177–179 °C; HRMS: Calcd for $\text{C}_{22}\text{H}_{18}\text{N}_4\text{O}_2\text{F}_3\text{S}$ [$M + H$]⁺ 459.1103, found 459.1083; δ_{H} (400 MHz, $(\text{CD}_3)_2\text{SO}$): 1.20 (3H, t, $J = 6.8$ Hz, CH_3), 4.07 (2H, q, $J = 6.8$ Hz, CH_2), 6.99 (1H, d, $J = 8.9$ Hz, Ar–H naph), 7.67–7.74 (4H, C_6H_4), 7.83 (1H, dd, $J = 8.9$ and 9.6 Hz, Ar–H naph), 8.44 (1H, d, $J = 8.2$ Hz, Ar–H), 8.52 (1H, d, $J = 7.5$ Hz, Ar–H naph), 8.70 (1H, d, $J = 7.5$ Hz, Ar–H naph), 9.92 (1H, s, NH), 10.32 (1H, s, NH), 10.36 (1H, s, NH); δ_{C} (100 MHz, $(\text{CD}_3)_2\text{SO}$): 13.3, 34.5, 105.6, 111.8, 119.5, 121.9, 125.0, 125.6, 125.8, 126.3, 128.9, 129.3, 130.9, 133.6, 142.8, 149.7, 162.8, 181.3; m/z 459 ($M + H$)⁺; $\nu_{\text{max}}/\text{cm}^{-1}$ 3483, 3254, 2980, 1686, 1647, 1616, 1586, 1535, 1387, 1325, 1245, 1165, 1116, 1066, 1017, 843, 776, 756.

6-[1-Amino-3-(*p*-tolyl)-thiourea]-2-ethylbenzo[de]isoquinoline-1,3-dione (2). **2** was synthesized according to the above procedure using **5** (0.20 g, 0.73 mmol) and *p*-tolyl isothiocyanate 97% (0.11 g, 0.73 mmol), yielding the desired product as a brown solid (0.05 g, 17%). mp 180–182 °C; HRMS: Calcd for $\text{C}_{22}\text{H}_{21}\text{N}_4\text{O}_2\text{S}$ [$M + H$]⁺ 405.1385, found 405.1383; δ_{H} (400 MHz, $(\text{CD}_3)_2\text{SO}$): 1.19 (3H, t, $J = 6.8$ Hz, CH_2CH_3), 2.26 (3H, s, $\text{C}_6\text{H}_4\text{CH}_3$), 4.08 (2H, q, $J = 6.8$ Hz, CH_2), 6.98 (1H, d, $J = 8.2$ Hz, Ar–H naph), 7.11 and 7.28 (4H, d, $J = 7.5$ Hz, C_6H_4), 7.78 (1H, dd, $J = 7.9$ and 8.2 Hz, Ar–H naph), 8.43 (1H, d, $J = 8.2$ Hz, Ar–H), 8.50 (1H, d, $J = 6.8$ Hz, Ar–H naph), 8.70 (1H, d, $J = 7.5$ Hz, Ar–H naph), 9.87 (1H, s, NH), 10.04 (1H, s, NH), 10.06 (1H, s, NH); δ_{C} (100 MHz, $(\text{CD}_3)_2\text{SO}$): 13.3, 20.5, 34.4, 105.4, 111.4, 119.4, 121.8, 124.8, 126.0, 128.4, 128.9, 129.5, 130.9, 133.7, 134.4, 136.5, 149.9, 162.8, 163.5, 181.3; m/z 405 ($M + H$)⁺; $\nu_{\text{max}}/\text{cm}^{-1}$ 3461, 3240, 2976, 1689, 1645, 1617, 1585, 1530, 1349, 1245, 1212, 1110, 1066, 1017, 915, 776, 756.

Acknowledgment. We thank Enterprise Ireland, TCD, IRCSET, and Wexford County Council for financial support. We also thank Dr. John E. O'Brien for assisting with NMR.

Supporting Information Available: Figures S1–S11. X-ray crystal data (CIF) for **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO0520487