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Fluorescence of Cyclopropenium Ion Derivatives

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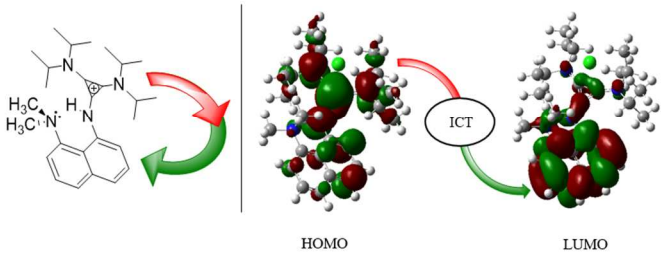
KEYWORDS: Cyclopropenium, Fluorescence, Charge Transfer, TD-DFT, Proton Sponge

ABSTRACT: The synthesis of cyclopropenium-substituted amino compounds and analysis of their photophysical properties is described. Systematic structural modifications of these derivatives lead to measurable and predictable changes in molar extinction coefficients, quantum yields, and Stokes shifts. Using time-dependent density functional theory (TD-DFT) calculations, the origin of these trends was traced to internal charge transfer (ICT) coupled with ensuing structural reorganization. Associated with this structural reorganization was an inward gearing of the cyclopropenium ring and twisting of the *peri*-NMe_2 group into co-planarity with the naphthalene ring system. Further, reinforcement of an intramolecular H-bond (IMHB) in the excited state alludes to a photo-induced spatiotemporal control of H-bonding for this proton sponge.



INTRODUCTION

Small molecule-based fluorophores play an integral part in day-to-day research, as light emitting diodes,[1,2,3] chemical sensors,[4,5,6] biological probes,[7] cellular imaging agents,[8] and light harvesting agents.[9] Their utility is broadened by their many mechanisms of action, such as Förster resonance energy transfer[10], photo-induced electron transfer,[11] aggregation and disaggregation-induced emission,[12,13] internal charge transfer,[14] and recently, motion-induced changes in emission.[15] Furthermore, their rapid photoactive response times, minimal disruption of local environments, and high sensitivity and visibility, makes them well-suited for monitoring real-time events with excellent spatial and temporal resolution.[16,17]

Currently, several classes of small organic fluorophores are commercially available. These fluorophores and their derivatives, however, often do not meet the desired photophysical and/or chemical properties needed for a given application. For this reason, new classes of small organic fluorophores are highly desirable, especially, if they expand the range of properties sought by consumers.

We recently reported a cyclopropenium-containing fluorophore, the Janus sponge (**1**),[18] which falls under the category of fluorophores containing a conjugated naphthalene π–system, such as dansyl amide (**2**), 4-aminonaphthaliamide (**3**), 1,2-benzo-3,4-dihydrocarbazole-9-ethyl chloroformate (**4**), and 6-Propionyl-2-(dimethylamino) naphthalene (**5**) (Figure 1). These naphthyl-based fluorophores (i.e., **2** – **5**) are known to derive their fluorescence from a donor-acceptor (D-A) charge transfer mechanism, wherein photoexcitation involves a transfer of charge from the nitrogen donor substituent to the naphthalene-based acceptor.[19,20]

Regardless of their classification, certain characteristics of organic fluorophores are universally useful: *i*) high molar extinction coefficients, *ii*) good photo and chemical stability, *iii*) high quantum yields, and *iv*) large Stokes shifts. The Janus sponge possesses these characteristics to varying degrees. For instance, **1** has a quantum yield (ϕ) of 0.37, a molar attenuation coefficient (ε) of 4.70 x 10^3 M^{-1} cm^{-1}, and a Stokes shift of 138 nm. Furthermore, **1** is stable, soluble, and fluorescent with both aqueous and organic solvents. Given these attributes, and its unique electronic and structural qualities outlined in our previous work, we envisioned that **1** could provide a scaffold for developing new, useful fluorescent organic molecules. Thus, we report herein the synthesis and photophysical analysis of systematically modified derivatives of this cyclopropenium-containing fluorophore, in conjunction with TD-DFT calculations, to provide mechanistic insight that will guide the future development of this new class of fluorophores.

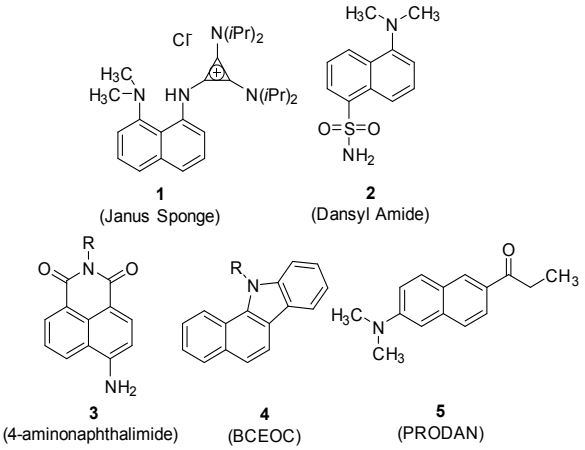


Figure 1. Selected naphthalene containing fluorescent organic molecule: Janus Sponge (**1**),[18] dansyl amide (**2**),[21] 4-aminonaphthalimide (**3**),[22] 1,2-benzo-3,4-dihydrocarbazole-9-ethyl chloroformate (BCEOC) (**4**),[23] 6-Propionyl-2-(dimethylamino) naphthalene (PRODAN) (**5**).[24]

RESULTS AND DISCUSSION

At the outset of this work, it was reasoned that the photophysical properties of compound **1** originated from the collective interactions of three defining structural components: namely, the cyclopropenium group, the (dimethyl)amine group, and the naphthalene backbone. Following this logic, each of these components were systematically modified, *via* the synthesis of **6** - **16**, and the impact on quantum yield, molar attenuation coefficient, absorbance maximum, emission maximum, and Stokes shift were recorded (Figure 2).

Modifications to the Cyclopropenium Group: (derivatives **6**, **7**, **16**)

Turning first to the dependency of the cyclopropenium group, compound **6** was used to gauge the impact of resonant lone pair donation from the nitrogen alkyl-substituents. Exchanging the *N*-diisopropyl substituents of **1** for *N*-dicyclohexyl groups resulted in a lower quantum yield ($\phi = 0.26$) and molar absorptivity, and a small bathochromic (red) shift in the absorption and emission maxima. The source of these changes was, in part, thought to derive from less effective nitrogen lone pair (LP) donation to the cyclopropenium π-system, owing to the greater flexibility of the *N*-dicyclohexyl substituents. This greater flexibility obstructs ideal alignment for η_{LP}-to-π_{aryl} orbital overlap, thus reducing the electron density of the cyclopropenium ring π-system, and with it, attenuating its donor capacity. Analog **7**, features a π-rich cyclopropenium substituent (*N*-diphenyl), and had a quantum yield of $\phi = 0.18$, a larger molar attenuation coefficient, and bathochromically shifted absorption ($\Delta\lambda = 9$ nm) and emission ($\Delta\lambda = 11$ nm) maxima. These trends are accounted for by competing nitrogen lone pair donation to the appended phenyl groups, rendering the cyclopropenyl-ring less electron rich, and/or localized donor-acceptor self-quenching. Meanwhile, removing the cyclopropenium unit altogether afforded compound **16**, which had a dramatically reduced quantum yield ($\phi = 0.13$), hypsochromic (blue) shifted absorption ($\Delta\lambda = 29$ nm) and emission ($\Delta\lambda = 56$ nm) maxima and a substantially smaller Stoke shift (111 nm), relative to **1**.

Taken together, these modifications to the cyclopropenium moiety demonstrate its vital role in luminescence. Decreasing the electron donating ability of the cyclopropenyl-amino groups, or increasing their electron withdrawing abilities, improves the photon absorption, while simultaneously impeding the fluorescence decay process (or facilitating the non-radiative decay processes). Furthermore, the difference between **5** and **16** shows that the cyclopropenium group drastically changes the quantum yield and Stokes shift of the aminonaphthalene core.

Modifications to the NMe_2 Group: (derivatives **8**, **9**, **10**, **11**).

Modifications to the NMe_2 group included fundamental electronic changes, tethering of the alkyl groups, positional isomerization, and removal of the amine altogether. To this end, exchange of the NMe_2 substituent for a *N*-*tert*-butyloxycarbonyl (*N*-Boc) group resulted in derivative **8** having a broad absorption band centered at 308 nm, with a shoulder displaying a maximum at 370 nm. Excitation at either 308 nm or 334 nm resulted in emission at 414 nm, while excitation at 361 nm manifested in an emission maximum at 448 nm, indicating the presence of two different fluorescent transitions.

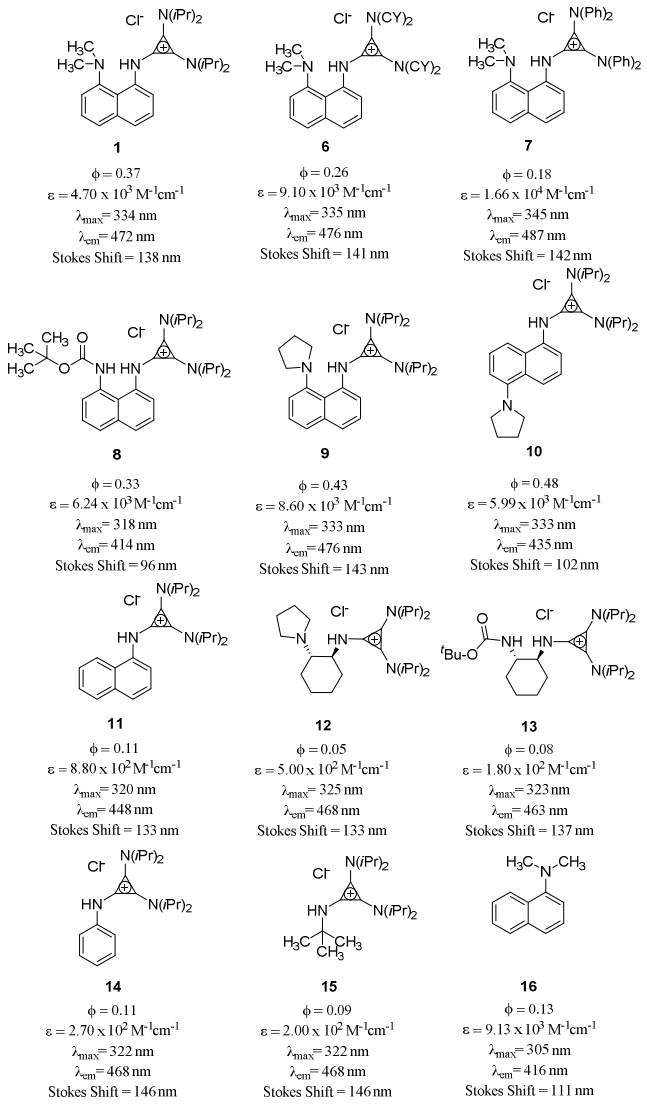


Figure 2. Prepared derivatives with spectroscopic profiles calculated in ethanol.

Nonetheless, derivative **8** showed a similar quantum yield ($\phi = 0.33$), relative to **1**, but a 42 nm lower Stokes shift. Incorporation of a pyrrolidine ring substituted compound **9** had an increased quantum yield ($\phi = 0.43$) of nearly 10 % and a slight bathochromically shifted emission maxima ($\Delta\lambda = 4$ nm), which in turn gave a marginally higher Stokes shift ($\Delta\lambda = 5$ nm). The spatial influence of the amine group, relative to the cyclopropenium group, was probed by preparing the 1,5-positional isomer compound **10**. This modification resulted in a larger quantum yield ($\phi = 0.48$) and a 37 nm lower emission maximum, resulting in a 36 nm decrease in Stokes shift. Removal of the amine group altogether as in compound **11** substantially reduced the quantum yield ($\phi = 0.11$), resulting in a hypsochromic shift in the absorption ($\Delta\lambda = 14$ nm) and emission ($\Delta\lambda = 24$ nm) values, and thus a smaller Stokes shift ($\Delta\lambda = 10$ nm).

These modifications to the NMe_2 group of **1** clearly showed its importance for luminescence. The increased quantum yield observed by modifying the NMe_2 group likely stems from non-radiative decay processes associated with rotational and vibrational degrees of freedom (such as those found in twisted

intramolecular charge transfer (TICT) states).[25, 26, 27] Supporting this premise were the enhanced quantum yields and other emissive properties of compounds **9** and **10**, in which the motion of the nitrogen was restricted by incorporation into a pyrrolidine ring. Moreover, the spatial relationship between the NMe_2 (or pyrrolidine) group and the cyclopropenium had a definitive influence on luminescence, undoubtedly owing to some combination of steric congestion (and thus restricted rotation) and direct non-covalent bonding interactions, such as an intramolecular hydrogen bond (IMHB).

Modifications to the Naphthalene Backbone: (derivatives **12**, **13**, **14**, **15**)

The importance of the naphthalene backbone was investigated by substitution for surrogates, which still maintained the close spatial relationship between the amine and cyclopropenium groups. To this end, pyrrolidine and *N*-Boc cyclohexyl functionalized compounds **12** and **13** revealed that removing the naphthalene backbone manifested in drastically reduced molar attenuation coefficients (5.0×10^2 $M^{-1}cm^{-1}$ and 1.8×10^2 $M^{-1}cm^{-1}$) and quantum yields ($\phi = 0.05$, $\phi = 0.08$). Despite this reduced luminescence character, there were only slight shifts in the absorbance and emission maxima of **12** and **13**, which retained large Stokes shifts of 143 nm and 137 nm. Similarly, the derivatives without the NMe_2 or naphthalene groups (*i.e.*, **14** and **15)** had low quantum yields ($\phi = 0.09$, $\phi = 0.11$) and low molar absorptivity, but exhibited only small hypsochromic shifts in absorbance and emission maxima, thus retaining large Stokes shift of 146 nm.

It is obvious from derivatives **12** – **15** that the conjugated naphthalene backbone is important for high molar extinction coefficients and high quantum yields. What is perhaps the most surprising result, however, is that while the aminonaphthyl group has beneficial photophysical effects, the fundamental transitions are still present in, and likely inherent to, the cyclopropenium core itself.

COMPUTATIONAL STUDIES

To gain insight into the electronic transitions of this class of fluorophores we performed time-dependent density functional theory (TD-DFT) calculations (Section 4 in Supporting Information) using compound **1** as a representative example (See Figure 3 for atom labels).

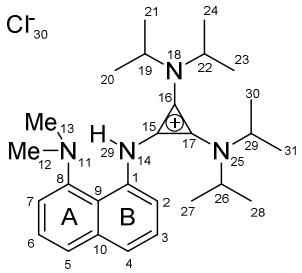
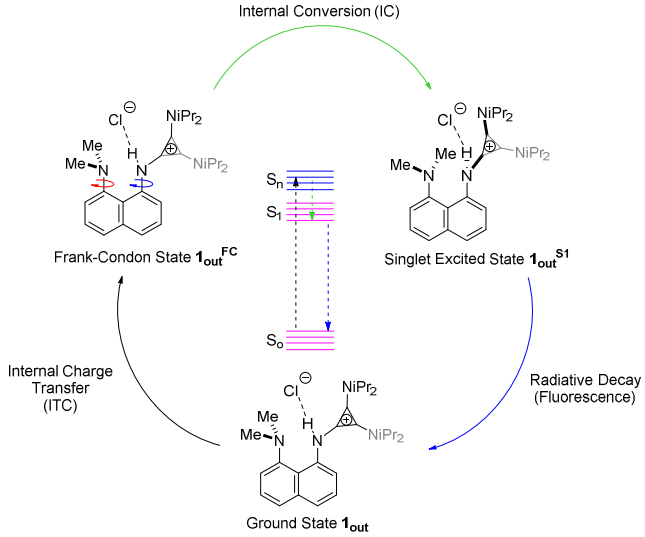


Figure 3. Two-dimensional representation of (**1**).

To this end, initial conformational searches provided several low-energy geometries that could be grouped into two categories, depending on if the N(14)-lone pair was facing inwards ($\mathbf{1_{In}}$) or outwards ($\mathbf{1_{out}}$), with the former being ~1.90 kcal mol^{-1} more stable (Figure 4). This energetic difference was influenced by an intramolecular N(11)···H(29) H-bond (d = 1.85 Å) present in $\mathbf{1_{In}}$, which was not present in $\mathbf{1_{Out}}$, where instead there was an intermolecular N(14)–H(29)···Cl(30) (d = 2.10 Å) H-bond. The energetic preference for $\mathbf{1_{In}}$ deserves mention as it is a structural homolog of $\mathbf{1_{Out}}$, which was the previously reported ground state structure of **1**.[18] This discrepancy, most likely, derives from differences in computational methodology, as the use of Grimme's D3 dispersion correction and Truhlar's M06-2X global hybrid functional used in this work provides a more accurate description of non-covalent interactions than B3LYP. Irrespective, given the small energetic difference between $\mathbf{1_{In}}$ and $\mathbf{1_{Out}}$, and the likelihood of their rapid interconversion, both conformers are considered.

The photophysical process of interest is generalized for conformer $\mathbf{1_{out}}$ in Scheme 1. Photon absorption from ground state (GS) $\mathbf{1_{out}}^{GS}$ affords the Frank-Condon (FC) state $\mathbf{1_{out}}^{FC}$, *via* an electronic reorganization. A nuclear and electronic relaxation process (*i.e.*, internal conversion (IC)), then yields the lower energy singlet excited (S_1) state $\mathbf{1_{out}}^{S1}$. Relaxation of the S_1 state back to the GS proceeds through a radiative or non-radiative decay process. Thus, the wavelength of the observed radiative decay (fluorescence) correlates with the free energy difference between the S_1 state and the GS. We discuss these transitions (shown in Figure 4), first for $\mathbf{1_{in}}^{S1}$, and then for $\mathbf{1_{out}}^{S1}$, below.



Scheme 1. Jablonski-type diagram, representing the general electronic transitions associated with the photoexcitation and emission of $\mathbf{1_{out}}$.

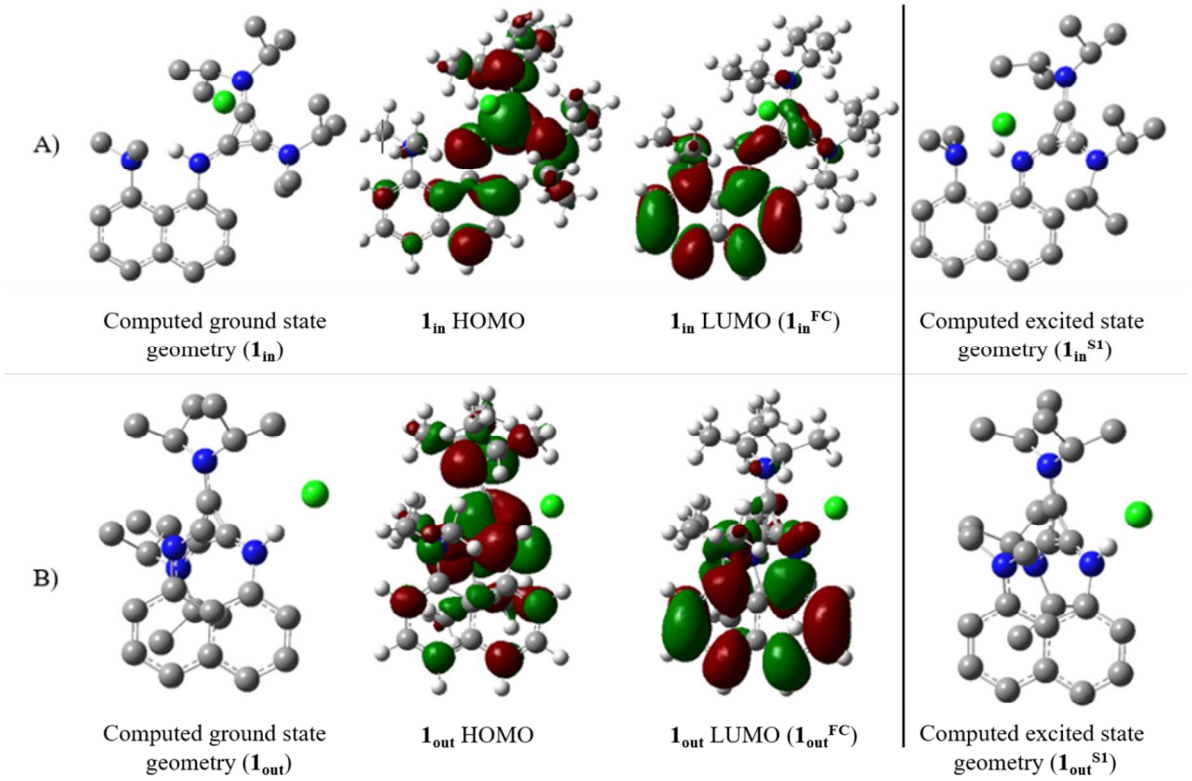


Figure 4. A) DFT computed geometry, HOMO, and LUMO of $\mathbf{1}_{In}$, as well as its TD-DFT optimized singlet excited state geometry. B) DFT computed geometry, HOMO, and LUMO of $\mathbf{1}_{out}$, as well as its TD-DFT optimized singlet excited state geometry. Level of theory: M062X-D3/6-31+g(d,p) scrf=(dichloromethane). Selected hydrogen atoms were removed for clarity.

We first computed the ultraviolet−visible (UV−vis) spectrum of $\mathbf{1}_{In}$, which had an absorbance maximum ($\lambda_{max,abs}$) at 312 nm (experimental $\lambda_{max,abs}$ = 334 nm) with an oscillator strength (*f*) of 0.4292, and a large dipole moment (δ = 12.48 Debye). A photoexcitation process involving a transition from the π_{HOMO}, where the electron density is largely located on the cyclopropenium ring, to the π_{LUMO}, which was located mainly on the naphthalene ring (Figure 4). Thus, in this internal charge transfer (ICT) process, the cyclopropenium, as opposed to the dimethylamine, acts as the primary donor group, while the naphthalene acts as the acceptor group.

The conformation of $\mathbf{1}_{in}^{S1}$ was dominated by two features (Figure 4): i) an inward gearing of the cyclopropenium and naphthalene rings towards co-planarity, and ii) a strengthened intramolecular H-bond (IMHB). The increased co-planarity was apparent from the dihedral angle between the two aromatic rings ($\Theta_{C(15)\text{-}N(14)\text{-}C(1)\text{-}C(9)}$ = 161.9 ° to 164.3 °), and likely originates from a preference for better π,π-orbital overlap leading to increased conjugation in the excited state. The increased strength of the IMHB in $\mathbf{1}_{in}^{S1}$ was apparent from a contracted N(14)−H(29)···N(11) H-bond distance (Δ*d* = ~0.24 Å) and a slightly elongated N(14)−H(29) H-bonded distance (Δ*d* = ~0.05 Å). Furthermore, the redistribution of electron density from nitrogen N(14) (Mulliken charges (*q*) = -0.206 eV to -0.088 eV) to the adjacent carbon atoms of the cyclopropenium (C(15) *q* = -0.396 eV to -0.567 eV) and naphthalene (C(1) *q* = 0.441 eV to 0.229 eV) rings, as well as increased electron density on N(11) (*q* = -0.604 eV to -0.775 eV), also supported a stronger IMHB. Quantum Theory of Atoms in Molecules (QTAIM) analysis of this N(14)−H(29)···N(11) H-bond revealed substantial increase in electron density (ρ) at the bond critical point (BCP) (Section 5 in the Supporting Information for details).

Associated with the formation of this IMHB and increased π-conjugation was a large observed Stokes shift. The TD-DFT computed structures show the emission as 384 nm (experimental = 472 nm), giving a computed Stokes shift of 72 nm (experimental = 132 nm). We ascribe these differences in computed and experimental Stokes shift values to limitations in explicitly accounting for solvent reorganization and other intermolecular vibrational energy redistribution pathways.

The computed UV−vis spectrum of $\mathbf{1}_{Out}$ had a $\lambda_{max,abs}$ of 319.2 nm and an oscillator strength (*f*) of 0.2535, which was noticeably smaller in magnitude than that of $\mathbf{1}_{in}$. Nevertheless, the photoexcitation was again dominated by a π_{HOMO}−π_{LUMO} based ICT processes (Figure 3), wherein electron density is transferred largely from the cyclopropenium ring, to the naphthalene ring. The relaxation from $\mathbf{1}_{out}^{FC}$ to $\mathbf{1}_{out}^{S1}$ also involved increased co-planarity between the cyclopropenium and naphthalene rings ($\Theta_{C(9)\text{-}C(1)\text{-}N(14)\text{-}C(15)}$ = -53.21 ° to -39.79 °). Because there is no IMHB in $\mathbf{1}_{out}$, this inward gearing of the cyclopropenium ring was coupled with twisting of the *peri*-NMe_2 group ($\Theta_{C(9)\text{-}C(8)\text{-}N(11)\text{-}C(12)}$ = -66.96 ° to -43.37 °) into conjugation with the naphthalene ring, resulting in nitrogen rehybridization to a $sp^{2.2}$-geometry and increased lone pair donation into the naphthalene ring π-system ($N_{11\ (LP)} \rightarrow C_7\text{-}C_{8\ (BD^*)}$, ΔE_{NBO} = 20.0 kcal mol^{-1}). This concerted motion led to a distortion of the aromatic naphthalene backbone from planari-

ty ($\Theta_{C(5)\text{-}C(10)\text{-}C(9)\text{-}C(1)}$= -172.4 °) and a 0.1 Å elongation of the N(11)···N(14) interatomic distance to 2.91 Å. In the absence of the IMHB, it appears that a larger increase in π-conjugation provided the stability associated with the large observed Stokes shift, which was computed to be 92 nm for $\mathbf{1}_{out}$[S1].

From these computed results, we can make several comparisons with the experimental data. From the compounds that share the same general structure as **1** (**6**, **7**, **8**, **9**, and **11**), we note that **8**, **10**, and **11** have significantly lower Stokes shifts, and that these compounds are all likely candidates to have greater co-planarity between the cyclopropenium and naphthalene rings in their ground states. This aligns qualitatively with the TD-DFT results, which indicate that the Stokes shift is, in part, a consequence of a change in this co-planarity during IC. It thus follows that pre-existing co-planarity would decrease the Stokes shift. Furthermore, the larger cyclopropenium-based π-system associated with **8** (due to the Ph-groups) is likely to be affected more strongly upon increased π-conjugation during IC, thus accounting for a higher Stokes shift. Lastly, we note the contribution of the cyclopropenium nitrogen groups in the HOMO and cyclopropenyl π-system in the LUMO, suggest that it can play the role of both the donor and the acceptor, in agreement with the experimental observation that the fluorescent transitions are inherent to the cyclopropenium core itself.

CONCLUSION

We have demonstrated, using systematic modifications, how the three key structural components of compound **1** (the cyclopropenium group, the (dimethyl)amine group, and the naphthalene backbone), influence its photophysical properties. By doing so, we found that cyclopropenium ions are inherently fluorescent, with large Stokes shifts. The understanding gained from this systematic study, together with the computational insight, provides us with the ability to rationally design new derivatives with targeted photophysical properties. More obvious modifications, such as extending the π-conjugation of the naphthalene acceptor group can increase the quantum yields, molar attenuation coefficients, Stokes shifts as well as red-shifting absorbance and emission wavelengths.[28, 29]

We expect that this new class of fluorescent cyclopropeniums will find utility in niche applications. The freebase of **1** is, in addition to being highly basic, poorly fluorescent, suggesting that it can be applied as a pH-responsive fluorescent probe at high pH-values (a range unavailable to most pH-dependent fluorescent probes). This class of cyclopropenium-functionalized amino containing derivatives[30,31] and cyclopropeniums in general[32] are also good metal-chelating ligands, and we thus expect **1** and its derivatives to have metal ion-dependent fluorescence properties. Given the high sensitivity of **1** to even subtle electronic perturbations, we expect that replacing H^+ with M^+ will have a drastic influence on fluorescence, which can lead to highly sensitive and metal-ion selective florescent probes.

EXPERIMENTAL SECTION

Computational Methodology

Calculations were carried out using Kohn-Sham Hybrid-Density Functional Theory (DFT) at the level of theory specified for each individual calculation. Geometry optimization were performed at standard temperature and pressure using Gaussian 09 and 16 programs and the resulting vibrational frequencies and molecular orbitals visualized with GaussView v5.0.8.[33] Natural bond orbital analysis (NBO Version 3.1[34] as implemented in Gaussian 09) was used to quantify the electronic donor-acceptor interactions as second-order perturbation energies (E_{NBO}). To account for solvent effects, the Integrated Equation Formalism Polarized Continuum Solvation Model (IEFPCM)[35] was used throughout the computations with default parameters for the chosen solvent(s). QTAIM calculations were computed using AIM2000.[36]

Materials and Methods

Materials were obtained from commercial suppliers and were used without further purification, unless otherwise specified. Dichloromethane (DCM) was distilled over CaH, tetrahydrofuran (THF) was distilled over Na and a benzophenone indicator, and acetonitrile (MeCN) was distilled over Na_2CO_3. Reactions were monitored by thin layer chromatography (TLC) using TLC silica gel 60 F254. NMR spectra were obtained with a 300 MHz spectrometer (^{1}H 300 MHz, ^{13}C 75.5 MHz or ^{13}C 150.9 MHz, ^{19}F 292.4 MHz, ^{11}B 96.3 MHz) or a 400MHz spectrometer. The chemical shifts are reported as δ values 105 (ppm) relative to tetramethylsilane. All reactions were performed under an inert nitrogen atmosphere. HRMS (high-resolution mass spectrometry) spectra were measured using electron ionization (EI), electrospray ionization (ESI) or fast atom bombardment (FAB) and a time-of-flight (TOF) mass analyzer in positive ionization mode. Absorption spectra were measured using a UV-Vis-NIR spectrophotometer at ambient temperature. Emission spectra were obtained on a Xenon flash lamp fluorescence spectrophotometer at ambient temperature with entrance and exit slit widths set to 5 mm.

N1-(2,3-bis(diisopropylamino)cycloprop-2-en-1-ylidene)-N8,N8-dimethylnaphthalene-1,8-diamine hydrochloride (Janus) (**1**).

To a solution of tetrachlorocyclopropene (0.025 mL, 0.2 mmol), in dichloromethane (2 mL) was added freshly distilled diisopropylamine (0.11 mL, 0.8 mmol) drop-wise under an inert nitrogen atmosphere. The reaction was stirred for four hours at room temperature, after which *N1,N1-dimethylnaphthalene-1,8-diamine* (**19**) (16 mg, 0.1 mmol) was added drop-wise as a solution in dichloromethane (2 mL) and the reaction was stirred for an additional 8 hours. The crude product was diluted with 5 mL of H_2O, quenched with 5 mL of 1 M HCl and extracted three times with 10 mL DCM. The combined organic extracts were dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product was purified by flash chromatography (11% methanol in DCM) to afford **1** as an off-white solid in 90% yield (59 mg, 0.08 mmol). m.p. = 225 °C – 230 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 13.81 (s, 1H), 7.74 – 7.71 (m, 1H), 7.55 – 7.50 (m, 3H), 7.44 – 7.38 (m, 1H), 6.97 (d, J = 7.0 Hz,1H), 4.03 – 3.94 (m, 4H), 2.84 (s, 6H) 1.41 (d, J = 6.75 Hz, 24H) 2.75 (s, 6H), 1.14 (d, J = 6.8 Hz, 24H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.3, 138.2, 136.2, 126.9, 126.7, 125.3, 123.2, 119.9, 119.4, 118.9, 112.3, 110.0, 51.4, 46.4, 22.1. HRMS (ESI): m/z calcd for $C_{27}H_{41}N_4$ (M+): 421.3326, found: 421.3331.

N1-(2,3-bis(dicyclohexylamino)cycloprop-2-en-1-ylidene)-N8,N8-dimethylnaphthalene-1,8-diamine hydrochloride (**6**).

To a solution of tetrachlorocyclopropene (35.6 mg, 0.2 mmol) in dichloromethane (2 mL) under an inert nitrogen atmosphere was added dicyclohexylamine (0.16 mL, 0.8 mmol). The reaction was stirred for four hours at room temperature, after which *N1,N1-dimethylnaphthalene-1,8-diamine* (**19**) (37.25 mg, 0.2 mmol) was added drop-wise as a solution in dichloromethane (2 mL) and the reaction was stirred for an addi-

tional 16 hours. The crude product was diluted with 5 mL of H_2O, quenched with 5 mL of 1 M HCl and extracted three times with 10 mL DCM. The combined organic extracts were dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography (11% methanol in DCM) to afford **6** as a white solid in 82% yield (123.1 mg, 0.18 mmol). m.p. = 125 °C – 129 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 13.07 (s, 1H), 7.70 – 7.73 (dd, J = 7.17, 2.17 Hz, 1H) (m,3H), 7.58 – 7.60 (d, J = 7.83 Hz, 1H), 7.47 – 7.54 (m, 2H), 7.39 – 7.44 (t, J = 7.83 Hz, 1H), 6.94 – 9.97 (d, J = 7.17, 1H), 3.93 - 3.47 (m, 1H), 2.82 (s, 6H), 1.84 – 1.94 (m, 16H), 1.49 - 1.68 (m, 12H), 1.21 – 1.34 (m, 8H), 1.03 – 1.07 (m, 4H).^{13}C-NMR (75 MHz, $CDCl_3$): δ = 150.3, 138.0, 136.3, 126.8, 125.7, 123.6, 121.13, 119.3, 118.9, 114.1, 110,5, 60.2, 46.6, 32.4, 25.6, 24.8. HRMS (EI): m/z calcd for C39H56N4 (M+): 580.4505, found: 580.4487.

N1-(2,3-bis(diphenylamino)cycloprop-2-en-1-ylidene)-N8,N8-dimethylnaphthalene-1,8-diamine hydrochloride (**7**).

To a solution of tetrachlorocyclopropene (35.6 mg, 0.2 mmol) in dichloromethane (2 mL) under an inert nitrogen atmosphere was added diphenylamine (0.11 mL, 0.8 mmol). The reaction was stirred for four hours at room temperature, after which *N1,N1-dimethylnaphthalene-1,8-diamine* (**19**) (37.3 mg, 0.2 mmol) was added drop-wise as a solution in dichloromethane (2 mL) and the reaction was stirred for an additional 16 hours. The crude product was diluted with 5 mL of H_2O, quenched with 5 mL of 1 M HCl and extracted three times with 10 mL DCM. The combined organic extracts were dried over MgSO4 and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography (11% methanol in DCM) to afford **7** as a white solid in 70% yield (83.5 mg, 0.14 mmol). m.p. = 138 °C – 140 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ =15.42 (s, 1H), 6.87–7.95 (m, 26H), 2.95 (s, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ =149.6, 142.8, 137.3, 136.8, 130.0, 129.6, 129.1, 127.1, 127.0, 125.8, 124.5, 124.1, 124.0, 119.7, 119.0, 116.8, 110.6, 46.34. HRMS (EI): m/z calcd for $C_{39}H_{32}N_4$ (M+): 556.2627, found: 556.2626.

tert-butyl (8-((2,3-bis(diisopropylamino)cycloprop-2-en-1 ylidene) amino)naphthalen-1-yl)carbamate hydrochloride (**8**).

To a solution of tetrachlorocyclopropene, (35.6 mg, 0.2 mmol) in dichloromethane (2 mL) under an inert nitrogen atmosphere was added diisopropylamine (0.11 mL, 0.8 mmol). The reaction was stirred for four hours at room temperature, after which *tert-butyl (8-aminonaphthalen-1-yl)carbamate* (**17**) (57.3 mg, 0.2 mmol) was added drop-wise as a solution in dichloromethane (2 mL) and the reaction was stirred for an additional 16 hours. The crude product was diluted with 5 mL of H_2O, quenched with 5 mL of 1 M HCl and extracted three times with 10 mL DCM. The combined organic extracts were dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography (11% methanol in DCM) to afford **8** as a light red solid in 90% yield (95.2 mg, 0.18 mmol). The solid decomposes before reaching its melting point. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 11.57 (s, 1H), 9.22 (s, 1H), 7.79 – 7.82 (dd, J = 7.82, 1.34 Hz, 1H), 7.71 – 7.73 (d, J = 7.94 Hz, 1H), 7.64 – 7.66 (d, J = 7.26 Hz, 1H), 7.45 – 7.51 (t, J = 7.89 Hz, 1H), 7.33 – 7.42 (m, 2H), 3.52 – 3.65 (m, 4H), 1.48 (s, 9H), 1.23 – 1.25 (d, J = 6.93 Hz, 24H).^{13}C-NMR (75 MHz, $CDCl_3$): δ = 155.1, 136.2, 134.9, 133.1, 129.2, 127.6, 127.3, 126.7, 126.6, 126.3, 124.7, 115.6, 114.0, 79.0, 50.7, 28.5, 22.0. HRMS (EI): m/z calcd for $C_{30}H_{44}N_4O_2$ (M+): 492.3464, found: 492.3448.

N1,N1,N2,N2-tetraisopropyl-3-((8-(pyrrolidin-1-yl) naphthalen-1-yl)imino) cycloprop-1-ene-1,2-diamine hydrochloride (**9**).

To a solution of tetrachlorocyclopropene, (35.6 mg, 0.2 mmol) in dichloromethane (2 mL) under an inert nitrogen atmosphere was added diisopropylamine (0.11 mL, 0.8 mmol). The reaction was stirred for four hours at room temperature, after which *8-(pyrrolidin-1-yl)naphthalen-1-amine* (**20**) (42.5 mg, 0.2 mmol) was added drop-wise as a solution in dichloromethane (2 mL) and the reaction was stirred for an additional 16 hours. The crude product was diluted with 5 mL of H_2O, quenched with 5 mL of 1 M HCl and extracted three times with 10 mL DCM. The combined organic extracts were dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography in (11% methanol in DCM) to afford **9** as a white solid in 91% yield (88.5 mg, 0.18 mmol). m.p. = 72 °C – 78 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 13.42 (s, 1H), 7.66 – 7.69 (dd, J = 7.32, 2.10 Hz, 1H), 7.43 – 7.54 (m, 3H), 7.35 – 7.40 (t, J = 7.51 Hz, 1H), 6.86 – 6.88 (dd, J = 7.35, 1.00 Hz, 1H), 3.86 – 3.99 (m, 4H), 3.38 (bs, 2H), 3.08 (bs, 2H), 2.14 (bs, 2H), 1.97 (bs, 2H), 1.34 – 1.36 (d, J = 6.78 Hz, 24H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ =148.5, 137.9, 136.0, 127.1, 125.2, 123.9, 120.4, 120.2, 119.9, 113.4, 110.6, 56.6, 51.5, 25.0, 22.3. HRMS (EI): m/z calcd for $C_{29}H_{43}N_4$ (M+): 447.3482, found: 447.3490.

N-(2,3-bis(2,4-dimethylpentan-3-yl)cycloprop-2-en-1-ylidene) -5-(pyrrolidin-1-yl)naphthalen-1-aminium chloride (**10**).

To a solution of tetrachlorocyclopropene (73.8 mg, 0.35 mmol) in dichloromethane (10 mL) under an inert nitrogen atmosphere was added diisopropylamine (0.21 mL, 1.47 mmol). The reaction was stirred for four hours at room temperature, after *5-(pyrrolidin-1-yl)naphthalen-1-amine* (**24**) (73.8 mg, 0.35 mmol), was added drop-wise as a solution in dichloromethane (4 mL) and the reaction was stirred for an additional 16 hours. The crude product was diluted with 5 mL of H_2O, quenched with 5 mL of 1 M HCl and extracted three times with 10 mL DCM. The combined organic extracts were dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography (11 % methanol in DCM) to afford **10** as a white solid in 95% yield (160.6 mg, 0.33 mmol). m.p. = 66 °C – 70 °C ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 11.14 (s, 1H), 8.05 (d, J = 8.68 Hz, 1H), 7.53 (d, J = 7.00 Hz, 1H), 7.41 (d, J = 8.68 Hz, 1H), 7.33 – 7.25 (m, 2H), 3.41 (m, 4H), 3.24 (m, 4H), 1.96 (m, 4H), 1.07 (d, J = 7.03 Hz, 24H).^{13}C-NMR (75 MHz, $CDCl_3$): δ = 148.2, 135.8, 131.8, 129.1, 126.9, 124.2, 123.8, 116.3, 115.9, 115.0, 112.1, 52.8, 50.7, 24.6, 21.8. HRMS (EI): m/z calcd for $C_{29}H_{43}N_4$ (M+): 447.3471, found: 447.3468.

N1,N1,N2,N2-tetraisopropyl-3-(naphthalen-1-ylimino)cycloprop-1-ene-1,2-diamine hydrochloride (**11**).

To a solution of tetrachlorocyclopropene, (35.6 mg, 0.2 mmol) in dichloromethane (2 mL) under an inert nitrogen atmosphere was added diisopropylamine (0.11 mL, 0.8 mmol). The reaction was stirred for four hours at room temperature, after which 1-naphthylamine (28.6 mg, 0.2 mmol) was added drop-wise as a solution in dichloromethane (2 mL) and the reaction was stirred for an additional 16 hours. The crude product was diluted with 5 mL of H_2O, quenched with 5 mL of 1 M HCl and extracted three times with 10 mL DCM. The combined organic extracts were dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product was puri-

fied by flash column chromatography (11% methanol in DCM) to afford **11** as a white solid in 95% yield (21.7 mg, 0.19 mmol). m.p. = 250 °C – 255 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 11.58 (s, 1H), 7.96 – 7.99 (dd, J = 6.22, 1.08 Hz, 1H), 7.80 – 7.83 (m, 1H), 7.70 – 7.73 (d, 8.32 Hz, 1H), 7.58 – 7.60 (d, J = 7.14 Hz, 1H), 7.37 – 752 (m, 3H) 3.42 – 3.56 (m, 4H), 1.12 – 1.14 (d, J = 6.89 Hz, 24H).^{13}C-NMR (75 MHz, $CDCl_3$): δ = 152.8, 134.7, 130.5, 127.3, 125.9, 125.2, 125.1, 124.7, 123.8, 118.6, 116.4, 113.7, 49.4, 22.3. HRMS (EI): m/z calcd for $C_{25}H_{35}N_3$ (M+): 377.2831, found: 377.2822.

N1-(2,3-bis(diisopropylamino)cycloprop-2-en-1-ylidene)-N2-pyridin-1-ylcyclohexane-1,2-diamine hydrochloride (**12**).

To a solution of tetrachlorocyclopropene, (35.6 mg, 0.2 mmol) in dichloromethane (2 mL) under an inert nitrogen atmosphere was added diisopropylamine (0.11 mL, 0.8 mmol). The reaction was stirred for four hours at room temperature, after which *(trans)-2-(pyrrolidin-1-yl)cyclohexanamine* (**23**) (33.6 mg, 0.2 mmol) was added drop-wise as a solution in dichloromethane (2 mL) and the reaction was stirred for an additional 8 hours. The crude product was diluted with 5 mL of H_2O, quenched with 5 mL of 1 M HCl and extracted three times with 10 mL DCM. The combined organic extracts were dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography (11% methanol in DCM) to afford **12** as a orange oil in 90% yield (790.4 mg, 1.8 mmol). ^{1}H-NMR (300 MHz, $CO(CD_3)_2$): δ = 4.04 (m, 4H), 3.50 (m, 1H), 3.30 (m, 1H), 2.80 (m, 4H), 2.09 (m, 4H), 1.58–1.87 (m, 8H), 1.36 (d, J = 6.82, 24H).^{13}C-NMR (75 MHz, $CO(CD_3)_2$): δ =117.4, 114.7 62.2, 60.3, 50.6, 48.5, 33.7, 24.7, 24.7, 23.3, 21.5, 21.2. HRMS (EI): m/z calcd for $C_{25}H_{47}N_4$ (M+): 403.3795, found: 403.3795.

tert-butyl ((1S,2S)-2-((2,3-bis(diisopropylamino)cycloprop-2-en-1-ylidene)amino)cyclohexyl)carbamate hydrochloride (**13**).

To a solution of tetrachlorocyclopropene, (35.6 mg, 0.2 mmol) in dichloromethane (2 mL) under an inert nitrogen atmosphere was added diisopropylamine (0.11 mL, 0.8 mmol). The reaction was stirred for four hours at room temperature, after which *tert-butyl ((trans)-2-aminocyclohexyl)carbamate*[37] (**21**) (33.6 mg, 0.2 mmol) was added drop-wise as a solution in dichloromethane (2 mL) and the reaction was stirred for an additional 8 hours. The crude product was diluted with 5 mL of H_2O, quenched with 5 mL of 1 M HCl and extracted three times with 10 mL DCM. The combined organic extracts were dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography (11% methanol in DCM) to afford **13** as a white solid in 90% yield (790.4 mg, 1.8 mmol). Product decomposes before its melting point, at 80 °C – 84 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.41 (bs, 1H), 6.17 (bs, 1H), 4.06 (m, 1H), 3.88 (m, 4H), 3.74 (m, 1H), 2.08 (m, 1H), 1.93 (m, 2H), 1.73 (m, 5H), 1.39 – 1.35 (m, 33H) .^{13}C-NMR (75 MHz, $CDCl_3$): δ = 156.6, 116.4, 113.3, 78.5, 59.7, 53.9, 50.5, 34.7, 30.7, 28.3, 25.1, 24.5, 22.2, 22.1 . HRMS (EI): m/z calcd for $C_{26}H_{49}N_4O_2$ (M+): 484.3544, found: 484.3548.

N-(2,3-bis(diisopropylamino)cycloprop-2-en-1-ylidene)benzenaminium chloride (**14**).[38]

To a solution of tetrachlorocyclopropene, (35.6 mg, 0.2 mmol) in dichloromethane (2 mL) under an inert nitrogen atmosphere was added diisopropylamine (0.11 mL, 0.8 mmol). The reaction was stirred for four hours at room temperature, after which aniline (18.6 mg, 0.2 mmol) was added drop-wise as a solution in dichloromethane (2 mL) and the reaction was stirred for an additional 8 hours. The crude product was diluted with 5 mL of H_2O, quenched with 5 mL of 1 M HCl and extracted three times with 10 mL DCM. The combined organic extracts were dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product was purified by crystallization in MeCN/EtOAc (1:1) to afford **14** as a white crystalline solid in 96% yield (69.9 mg, 0.19 mmol). m.p. = 188 °C – 190 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 11.69 (s, 1H), 7.41 – 7.45 (m, 2H), 7.30 – 7.35 (m, 2H), 7.10 – 7.15 (m, 1H), 3.75 – 3.89 (m, 4H), 1.34 – 1.37 (d, J = 6.83 Hz, 24H).^{13}C-NMR (75 MHz, $CDCl_3$): δ = 139.5, 130.0, 126.4, 123.2, 117.1, 112.9, 51.4, 22.2. HRMS (EI): m/z calcd for $C_{21}H_{34}N_3$ (M+): 328.2736, found: 328.2753.

3-(tert-butylimino)-N1,N1,N2,N2-tetraisopropylcycloprop-1-ene-1,2-diamine hydrochloride (**15**).[39]

To a solution of tetrachlorocyclopropene, (35.6 mg, 0.2 mmol) in dichloromethane (2 mL) under an inert nitrogen atmosphere was added diisopropylamine (0.11 mL, 0.8 mmol). The reaction was stirred for four hours at room temperature, after which *tert*-butylamine (14.6 mg, 0.2 mmol) was added drop-wise as a solution in dichloromethane (2 mL) and the reaction was stirred for an additional 8 hours. The crude product was diluted with 5 mL of H_2O, quenched with 5 mL of 1 M HCl and extracted three times with 10 mL DCM. The combined organic extracts were dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product was purified by crystallization in MeCN/EtOAc (1:1) to afford **15** as a white crystalline solid in 98% yield (67.4 mg, 0.2 mmol). m.p. = 171 °C – 172 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.99 – 4.08 (m, 4H), 1.49 (s, 9H), 1.34 – 1.37 (d, J = 6.82, 24H).^{13}C-NMR (75 MHz, $CDCl_3$): δ = 118.0, 116.8, 53.3, 51.0, 30.3, 22.5. HRMS (EI): m/z calcd for $C_{19}H_{38}N_3$ (M+): 308.3049, found: 308.3069.

N,N-dimethylnaphthalen-1-amine (**16**).[40]

To a 100 mL round bottom flask containing 1-napthylamine (100 mg, 0.70 mmol), was added Na_2CO_3 (386 mg, 4.60 mmol), fitted with a reflux condenser, flame-dried, and backfilled with $N_{2(g)}$. Acetonitrile (20 mL) was then added, followed by the drop-wise addition of freshly distilled Me_2SO_4 (0.46 mL, 4.90 mmol). The reaction mixture was heated to reflux, and stirred for 16 hours. The mixture was then concentrated under reduced pressure, diluted with 20 mL of H_2O, and extracted three times with 10 mL of dichloromethane. The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. Purified compound could be acquired by flash column chromatography (12.5% ethyl acetate in hexanes). The final product was isolated as a light brown liquid in 18% yield (21.2 mg, 0.12 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.24 – 8.27 (d, 1H, J = 9.5 Hz), 7.82 – 7.85 (d, 1H, J = 7.5 Hz), 7.39 - 7.55 (m, 3H), 7.44 – 7.47 (t, 1H, J = 7.8 Hz), 7.08 – 7.11 (d, 1H, J = 7.5 Hz), 2.93 (s, 6H).

tert-butyl (8-aminonaphthalen-1-yl)carbamate (**17**).[41]

To a flame dried 100 mL round bottom flask backfilled with $N_{2(g)}$ was added 1,8-diaminonaphthalene (2.0 g, 12.6 mmol), followed by the addition of THF (40 mL) and NEt_3 (2 mL, 27.2 mmol). To the resulting mixture a solution of di-*tert*-butyl-dicarbonate (3.0 g, 13.9 mmol) in THF (10 mL) was added drop-wise over two hours *via* syringe pump and allowed to stir at room temperature for 18 hours. THF was removed under reduced pressure and the crude product mixture was dissolved in toluene (20 mL), washed sequentially with 1 M NaOH (20 mL), brine (20 mL), and distilled H_2O (20 mL). The organic layer was subsequently dried over $MgSO_4$ and

concentrated under reduced pressure. After purification by flash column chromatography (20% ethyl acetate in hexanes), the final product was isolated as red crystals in 84% yield. m.p. = 77 °C - 81 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.79 (s, 1H), 8.08 (d, J = 7.3 Hz, 1H), 7.49 (t, J = 7.7 Hz, 1H), 7.40 (m, 2H), 7.22 (t, J = 7.7, 1H), 6.78 (d, J = 7.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.3, 140.9, 136.3, 135.5, 126.1, 125.6, 123.6, 122.7, 118.9, 116.9, 116.8, 80.2, 28.5. HRMS (EI): m/z calcd for $C_{15}H_{18}N_2O_2$ (M+): 258.1308, found: 258.1366.

tert-butyl(8-(dimethylamino)naphthalene-1-yl)carbamate (**18**).

To a 100 mL round bottom flask containing *tert-butyl (8-aminonaphthalen-1-yl)carbamate* (**17**) (100 mg, 0.38 mmol), was added Na_2CO_3 (210 mg, 2.51 mmol), fitted with a reflux condenser, flame-dried, and backfilled with $N_{2(g)}$. Acetonitrile (10 mL) was then added, followed by the drop-wise addition of freshly distilled Me_2SO_4 (0.26 mL, 2.69 mmol). The reaction mixture was heated to reflux, and stirred for 16 hours. The mixture was then concentrated under reduced pressure, diluted with 20 mL of H_2O, and extracted three times with 10 mL of dichloromethane. The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. Purified compound could be acquired by flash column chromatography (12.5% ethyl acetate in hexanes). The final product was isolated as a clear oil in 70% yield (3.4 mmol, 0.98 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 12.79 (s, 1H), 8.35-8.32 (dd, J = 7.0, 2.3 Hz, 1H), 7.62 (d, J = 8 Hz, 1H), 7.45-7.27 (m, 4H), 2.81 (s, 6H), 1.58 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.7, 150.3, 137.0, 136.1, 126.4, 125.3, 122.0, 119.3, 117.6, 114.1, 79.2, 45.9, 28.5. HRMS (ESI): m/z calcd for $C_{17}H_{22}N_2O_2$ (M+H)+: 287.1754, found: 287.1748.

N1,N1-dimethylnaphthalene-1,8-diamine (**19**).

To a 50 mL round bottom flask containing *tert-butyl (8-(dimethylamino)naphthalen-1-yl)carbamate* (**18**) (250 mg, 0.873 mmol), backfilled with $N_{2(g)}$, was added DCM (15 mL). To the resulting mixture was added trifluoroacetic acid (0.67 mL, 8.73 mmol) of trifluoroacetic acid was added drop-wise and the reaction was allowed to stir for 16 hours at room temperature. The crude product was diluted with 10 mL of H_2O, neutralized with 1 M NaOH and extracted three times with 10 mL of dichloromethane. The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. Purified compound could be acquired by flash chromatography (11% ethyl acetate in hexanes). **19** was obtained as a brown oil in a 90% yield (0.830 mmol, 154.5 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80 – 7.70 (d, J = 7.8 Hz, 1H), 7.54 - 7.45 (m, 2H), 7.40 - 7.37 (d, J = 7.6 Hz, 1H), 7.33 - 7.30 (d, J = 7.6 Hz, 1H), 6.80 - 6.78 (d, J = 7.6 Hz, 1H), 6.33 (bs, 2H), 2.93 (s, 6H). ^{13}C NMR (75 MHz, CDCl3): δ = 152.1, 145.5, 137.0, 126.6, 125.4, 125.4, 118.7, 117.0, 115.1, 109.7, 46.2 HRMS (ESI): m/z calcd for $C_{12}H_{15}N_2$ (M+H)+: 187.1230, found: 187.1239.

8-(pyrrolidin-1-yl)naphthale-1-amine (**20**).

A 50 mL RBF containing Na_2CO_3 (455 mg, 4.2 mmol), fitted with a reflux condenser, was flame-dried and backfilled with N_2(g). A solution of 1,8-diaminonaphthalene (316.2 mg, 2.0 mmol) in DMF (5 mL) was then added under the inert nitrogen atmosphere, followed by 1,4-dibromobutane (0.24 mL, 2.0 mmol). The reaction was heated to 60 °C for 48 hours. The crude reaction mixture was partitioned between H_2O (15 mL) and DCM (15 mL). The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The product was purified by flash column chromatography (20% ethyl acetate in hexanes) to afford **20** as a dark brown oil in 24% yield (101.9 mg, 0.48 mmol). ^{1}H-NMR (300 MHz, CDCl3): δ = 7.50 – 7.53 (dd, J = 9.12, 1.10 Hz, 1H), 7.14 – 7.34 (m, 4H), 6.60 – 6.63 (dd, J = 7.37, 1.17 Hz, 1H), 6.15 (bs, 2H), 3.45 – 3.49 (m, 2H), 2.80 – 2.87 (m, 2H), 2.00 – 2.04 (m, 4H). ^{13}C-NMR (75 MHz, CDCl3): δ = 148.5, 137.9, 136.0, 127.1, 126.7, 125.2, 123.9, 121.0, 120.4, 120.2, 119.9, 113.4, 110.6, 56.6, 51.5, 25.0, 22.3. HRMS (EI): m/z calcd for C14H16N2 (M+): 212.1314, found: 212.1309.

tert-butyl ((trans)-2-aminocyclohexyl)carbamate (**21**).[37]

To a 50 mL RBF, flame-dried and backfilled with $N_{2(g)}$, was added 1,2-*trans*-diaminocyclohexane (0.48 mL, 4.0 mmol), and 10 mL DCM. The reaction was cooled to 0 °C in an ice bath, and a solution of di-*tert*-butyl dicarbonate (Boc_2O, 436.5 mg, 2.0 mmol) in DCM (8 mL) was added over two hours *via* syringe pump. The reaction was stirred for an additional 3 hours at room temperature. The reaction mixture was diluted with H_2O (10 mL) acidified to pH 5 with 1 M HCl and the organic layer extracted with Et_2O (10 mL). The aqueous layer was then basified to pH 10 with 1 M NaOH and extracted three times with 10 mL EtOAc. The combined EtOAc extracts were dried over $MgSO_4$ and concentrated *in vacuo*. The product was obtained in sufficiently pure form as a white solid in 35% yield (300.0 mg, 1.4 mmol). m.p. = 113 °C - 115 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.67 (bs, 1H), 3.02 – 3.12 (m, 1H), 2.33 – 2.31 (m, 1H), 1.88 – 1.97 (m, 2H), 1.63 – 1.67 (dt, J = 9.63, 2.69 Hz, 2H), 1.40 (s, 9H), 1.04 – 1.31 (m, 6H).^{13}C-NMR (75 MHz, $CDCl_3$): δ = 157.4, 78.9, 57.1, 54.4, 33.9, 32.6, 27.9, 25.3, 25.1.

tert-butyl ((trans)-2-(pyrrolidin-1-yl)cyclohexyl)carbamate (**22**).

A 50 mL RBF containing Na_2CO_3 (296.8 mg, 2.8 mmol), fitted with a reflux condenser, was flame-dried and backfilled with $N_{2(g)}$. *tert-butyl ((1R,2R)-2-aminocyclohexyl)carbamate* (**21**) (300.0 mg, 1.4 mmol), DMF (5 mL), and 1,4-dibromobutane (0.17 mL, 1.4 mmol) were then added and the reaction was heated to 60 °C for 24 hours. The crude reaction mixture was partitioned between H_2O (15 mL) and DCM (15 mL). The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The product was purified by flash column chromatography (5% methanol in DCM) to afford **22** as an orange oil in 90% yield (338.14 mg, 1.26 mmol). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.22 (bs, 1H), 3.27 – 2.22 (m, 1H), 2.60 – 2.64 (m, 2H), 2.50 – 2.56 (m, 2H), 2.34 – 2.44 (m, 2H), 1.70 – 1.79 (m, 6H), 1.45 (s, 9H), 1.10 – 1.39 (m, 4H).^{13}C-NMR (75 MHz, $CDCl_3$): δ = 156.0, 78.9, 62.3, 52.1, 47.9, 32.2, 28.3, 24.2, 24.0, 23.6, 23.2.HRMS (EI): m/z calcd for $C_{15}H_{28}N_2O_2$ (M+): 268.2151, found: 268.2149.

(trans)-2-(pyrrolidin-1-yl)cyclohexanamine (**23**).

To a 50 mL round bottom flask containing *tert-butyl ((trans)-2-(pyrrolidin-1-yl)cyclohexyl)carbamate* (**22**) (214.7 mg, 1.12 mmol), backfilled with $N_{2(g)}$, was added was added DCM (15 mL), followed by drop-wise addition of trifluoroacetic acid (0.86 mL, 11.2 mmol). The reaction was stirred at room temperature for 16 hours. The crude product was diluted with H_2O (10 mL), basified to pH 10 with 1M NaOH and extracted 3x with 10 mL DCM. The combined organic extracts were dried over $MgSO_4$ an concentrated *in vacuo*. The product was purified by flash column chromatography (11% ethyl acetate in hexanes) to afford **23** as a brown oil in a 90% yield (170.0 mg, 1.01 mmol). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.32–2.66 (m, 4H), 2.26 (m, 1H), 1.95 (m, 1H), 1.69–1.97 (m, 8H), 1.33 (m, 4H).^{13}C-NMR (75 MHz, $CDCl_3$): δ = 65.2, 52.8, 47.1, 35.0,

25.5, 25.0, 23.8, 21.5. HRMS (EI): m/z calcd for $C_{10}H_{20}N_2$ (M+): 168.1627, found: 168.1620.

5-(pyrrolidin-1yl)naphthalen-1-amine (**24**).

To a solution of 1,5-diaminonaphthalene (200 mg, 1.26 mmol) in dimethylformamide (20 mL) under an inert nitrogen atmosphere was added Na_2CO_3 (265 mg, 2.5 mmol) 1,4-dibromobutane (0.075 mL, 0.63 mmol). The reaction was fitted with a reflux condenser and heated to 60 °C for 16 hours. The crude product was diluted with 50 mL of H_2O and extracted three times with 20 mL DCM. The combined organic extracts were dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography (33.3 % ethyl acetate in hexanes) to afford **24** as a light brown oil in 55% yield (73.8 mg, 0.35 mmol). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.77 (d, J = 8.67 Hz, 1H), 7.49 (d, J = 8.48 Hz, 1H), 7.41 (t, J = 7.88 Hz, 1H), 7.34 – 7.30 (m, 1H), 7.07 (dd, J = 7.46, 1.01 Hz, 1H) 6.80 (dd, J = 7.46, 0.92 Hz, 1H), 4.08 (bs, 2H), 3.40 (m, 4H) 2.07 (m, 4H).^{13}C-NMR (75 MHz, $CDCl_3$): δ =148.3, 142.4, 129.3, 125.2, 125.0, 124.8, 115.9, 114.2, 111.0, 109.8, 52.8, 24.8. HRMS (EI): m/z calcd for $C_{14}H_{16}N_2$ (M+): 212.1314, found: 212.1321.

ASSOCIATED CONTENT

^{1}H-NMR and ^{13}C-NMR spectra. Computational methodology and coordinate/thermochemical data for all computed structures. QTAIM and NBO analyses. Protocol for the quantum yield measurements. Absorbance and Emittance data for all derivatives. This material is available free of charge via the Internet at http://pubs.acs.org.

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