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Dynamic proton-induced two-stage emission switching in donor-functionalized bis(dehydrobenzo[*n*]annuleno)benzenes and 1,2,4,5-tetrakis(phenylethynyl)benzene

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Titration of three electron donor-functionalized bis(dehydrobenzo[*n*]annuleno)benzenes and a corresponding acyclic 1,2,4,5-tetrakis(phenylethynyl)benzene derivative with trifluoroacetic acid in CH_2Cl_2 resulted in two-stage emission switching behavior in which initial acidification caused bathochromic shifts, followed by dramatic hypsochromic shifts upon further addition of acid. Differences in the various spectra are rationalized by structure and chromophore architecture. The results indicate independent manipulation of frontier molecular orbital energy levels by stepwise ion addition, therefore suggesting transient and tunable intramolecular charge transfer systems upon partial protonation.

1. Introduction

Conjugated fluorophores rich in π-electrons have been recognized as ideal candidates for organic materials, organic electronics components, non-linear optical materials, and fluorescent sensor dyes.[1–9] Small structural variations in a particular molecular architecture can elucidate important structure–property relationships essential for fine-tuning the photophysical spectroscopic profiles to targeted applications.[4,9] To that end, we have been investigating the π-electronic behavior of a class of carbon-rich conjugated chromophores, dehydrobenzo-[*n*]annulenes (DBAs).[4,10] These carbocyclic molecules contain multiple pathways for intramolecular electronic and photonic transports and exhibit enhanced π-orbital overlap due to enforced planarization, often leading to bulk organic material behavior. For example, we have recently demonstrated the formation of ordered self-assembled monolayers of 18-membered DBA derivatives visualized at the liquid–solid interface via STM imaging,[4i] and have shown the ability of large DBA networks to approximate the materials properties of certain theoretical carbon allotropes.[4e] Furthermore, we have shown that functionalization with strong electron-donating groups results in low-lying excited states that provide efficient emission and are highly sensitive to molecular and electronic environments. We[4c,f] and others[9a,b] have reported several planarized DBA systems, as well as analogous acyclic arylacetylenes (e.g., **1** and **2**, Fig. 1), that exhibit an intriguing ability to switch their emissive wavelengths in one direction or the other based on independent manipulation of the energy levels of the frontier molecular orbitals (FMOs) through the titrimetric introduction of ions. In the conjugated acyclic systems,[4c,9a,b] the effect relied on donor/acceptor functionalization, with the calculated localizations of the HOMO and LUMO on the donor and acceptor segments, respectively. In the case of our recently examined pyridine-derivatized DBAs,[4f] the effect was observed even though the FMOs were predicted to mostly overlap. Herein, we report similar dynamic emission switching via acid titration of a series of solely donor-functionalized bis(dehydrobenzo-[*n*]annuleno)benzenes possessing 14-, 15-, and 18-membered rings along with an acyclic 1,2,4,5-tetrakis(phenylethynyl)benzene (TPEB) analogues (**1**–**4**, Fig. 1).

2. Results and discussion

In our previous studies, emission switching was caused by stepwise protonation (or in some cases, metal ion complexation) of first one type of group (donor or acceptor, depending on the structure), causing a dramatic red or blue shift in the fluorescence spectrum, followed by protonation of the other group with further addition of ion, causing a shift in the opposite direction.[4c,f] Here, only donating dibutylamino (Bu_2N) groups are present, so protonation may not proceed in a site-specific, stepwise fashion, but

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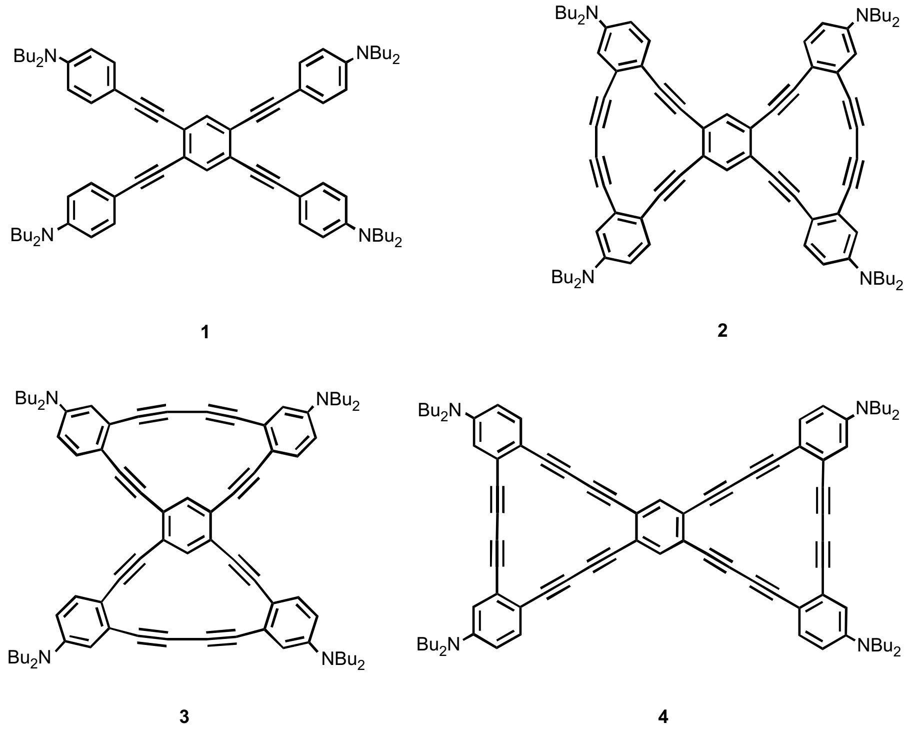


Figure 1. Donor-functionalized TPEB **1** and planarized bisDBAs **2**–**4**.

protonation of one or more of the nitrogens (thus generating a positively charged inductive *acceptor* unit) may still result in a transient donor/acceptor system with intramolecular charge transfer-like behavior. Examining the response of structurally similar compounds **1**–**4**[4a,h] should allow us to probe the individual effects of planarization, ring size, ring strain, and conjugation pathway efficiency.

Accordingly, dilute solutions of **1**–**4** in CH_2Cl_2 (1.0 mL, ca. 20 μM) were prepared with varying concentrations of trifluoroacetic acid (TFA) ranging from 10^{-5} to $10^{-0.3}$ M, and the effects on the excitation and emission spectra were observed (Fig. 2). No shifting of the peaks was observed for TFA concentrations between 0 and 10^{-5} M. For each spectrum, the excitation wavelength corresponding to maximal emission intensity was used. In each case, initial addition of TFA caused a 20–79 nm red shift in the emission with a qualitative loss of fluorescent intensity (Table 1). Compounds **1** and **2** experienced the greatest shifting between 10^{-5} and 10^{-2} M TFA, and **3** red-shifted the least. TPEB **1** attained its most bathochromic state at about 10^{-3} M TFA, fading from a bright blue-green to a less intense yellow. BisDBAs **2**–**4** required slightly more acidic conditions, reaching their most bathochromic states closer to 10^{-2} M TFA. BisDBA **3** shifted from green to yellow-orange, but **2** and **4** emitted an unusual fluorescent pink color from dual red-blue emission. With further TFA addition, new, dramatically blue-shifted ($\Delta\lambda$=75–168 nm) bands (or set of bands) were generated. TPEB **1** became a pale salmon-pink color similar to **2** and **4** as the hypsochromic bands increased in intensity. Since **3** experienced the least shifting in each stage, the overlapping bands at $10^{-2.1}$ M TFA generated fluorescence of comparable intensity over most of the visible range, resulting in nearly white emission. Additional TFA suppressed the bathochromic band in all molecules leading to blue or purple fluorescence, with spectra similar in appearance to their respective decyl- or non-functionalized parent analogues.[4a,g] The vibronic fine structure is typical of $\pi\rightarrow\pi^*$ transitions for these systems. Molecules **1** and **2** displayed the most hypsochromic spectra, with borderline UV emission at the highest TFA concentration, whereas **4** exhibited the greatest change in λ_{max}. In all cases, the most hypsochromic bands were of similar intensities to the neutral compound. It is believed that the protonation events are logarithmic rather than stoichiometric, since, for example, the 10^{-4}, 10^{-3}, and 10^{-2} M TFA solutions (which are 1.0 mL solutions containing 20 nmol analyte) represent 5, 50, and 500 equiv of acid, respectively, and this is the range over which the shifting occurs.

In the excitation spectra, the bands were quenched with slight to moderate red-shifting, until replaced by dramatically blue-shifted bands that grew in intensity as TFA concentration increased. The changes in the absorption spectra generally reflected the excitation spectra (see Supplementary data, Fig. S1). The most acidic solutions of **1**–**4** exhibited excitation band shapes similar to the absorption profiles of their corresponding decyl-functionalized analogues, providing strong support for an electron-deficient tetraprotonated state with only $\pi\rightarrow\pi^*$ transitions. For all systems, addition of *i*-Pr_2NH reversed the protonation to regenerate the original spectra, albeit at lower relative intensities, due to quenching by the resultant salts in solution (Supplementary data, Fig. S2).

The shifting behavior observed herein is the result of an incremental protonation of the donor moieties on the molecules. When only one, two, or three of the four donors are protonated, a cationic 'acceptor' substituent is generated, and an intramolecular charge transfer (ICT) state is accessed with localization of HOMO density on the unprotonated Bu_2N-functionlized segments and LUMO density on the protonated Bu_2NH^+ segments. Red-shifting in the absorption spectra and partial quenching of the lowest-energy band typically accompanies such functionalization relative to non- or donor-functionalized analogues. Similarly, in the emission spectra the energy of the lowest vibrational levels of the S_1 state decrease, causing a red shift as well.

In acyclic TPEB **1**, the most bathochromically shifted emission (λ_{max}=558 nm) occurs at about 10^{-3} M TFA, while **2**–**4** require almost another 10-fold increase in [TFA]. This increased basicity is likely due to the lack of co-planarity of the system; the peripheral donor arenes are calculated to be about 30° out of the plane of the central arene.[4a] The lone pairs on the nitrogens are therefore less

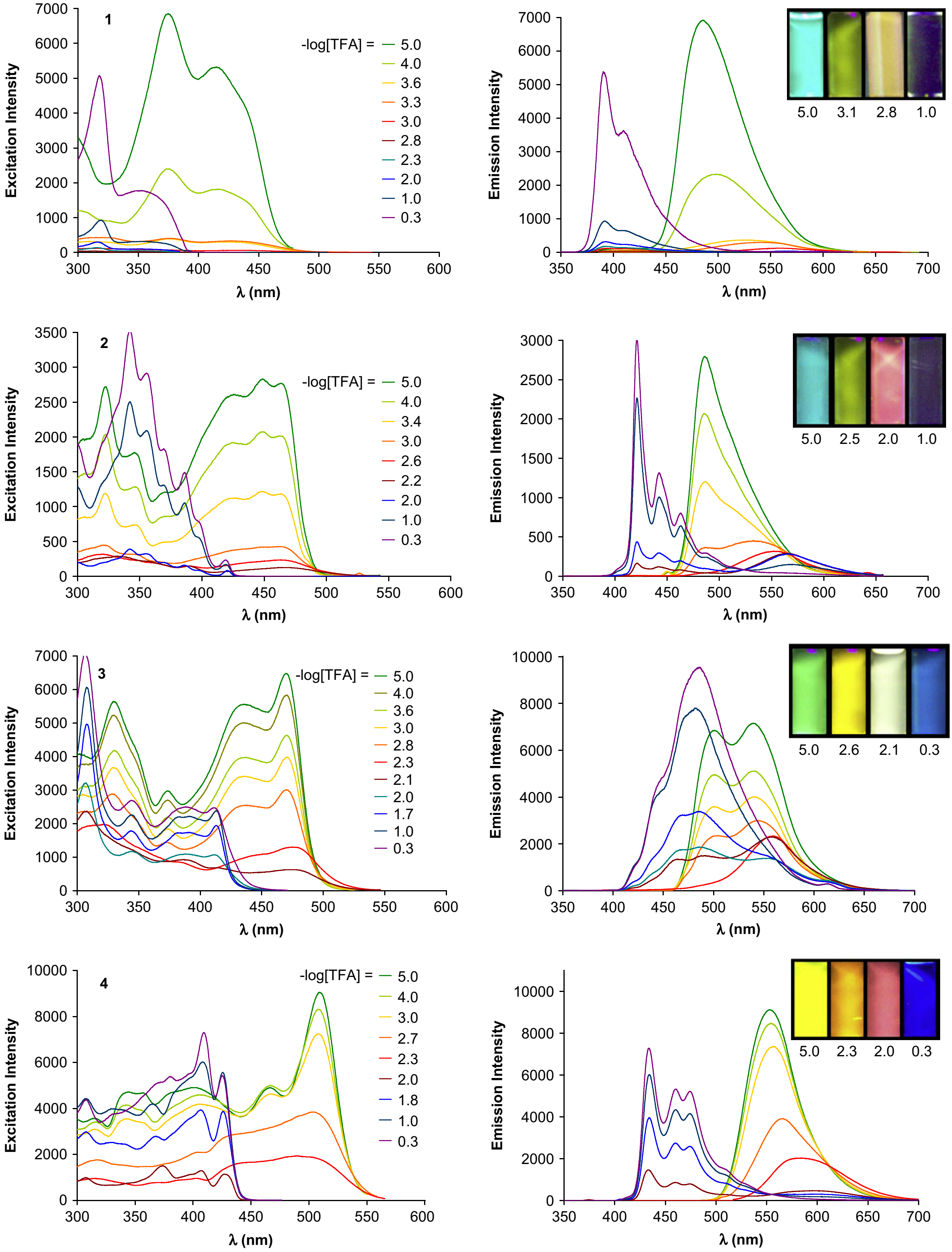


Figure 2. Excitation (left) and emission (right) spectra of TFA titration of **1**–**4** (top to bottom) in CH_2Cl_2 (ca. 20 μM). Insets: photographs of vials of analyte solutions at indicated −log[TFA] under illumination by high-intensity 365 nm lamp.

delocalized into the phenylacetylene network and are thus easier to protonate. Additionally, the unrestricted bond rotation may allow for relaxation to a twisted intramolecular charge transfer (TICT) state, with enhanced rates for non-radiative decay relative to **2**–**4**, which have enforced macrocycle co-planarity. There is one very low-intensity iso-emissive point at 518 nm shared by the spectra of solutions between $10^{-2.8}$ and $10^{-1.0}$ M TFA. There are no such points in spectra at lower TFA concentrations, which imply that the first three donor groups are protonated almost independently in rapid equilibrium. This was also observed for our donor/acceptor

Table 1
Summary of TFA-induced spectral shifting in **1**–**4**

−log[TFA]	**1**[a]		**2**[a]		**3**[a]		**4**[a]	
	λ_{ex} (nm)	λ_{em} (nm)	λ_{ex} (nm)	λ_{em} (nm)	λ_{ex} (nm)	λ_{em} (nm)	λ_{ex} (nm)	λ_{em} (nm)
No TFA	376	484	450	486	472	541, 502[b]	511	552
5.0	376	485	450	486	472	541, 502[b]	511	553
4.0	376	500	450	487	472	541, 502[b]	510	556
3.6	377	528			472	542, 502[b]		
3.4			450	488				
3.3	377	545						
3.0	316	558, 394[b]	463	536	472	543, 503[b]	510	558
2.8	316	394			472	544, 503[b]		
2.7							506	567
2.6			464	556				
2.3	317	394			322	558	489	584
2.2			467	565, 421[b]				
2.1					308	561, 488[b]		
2.0	317	394	344	565	308	561, 488[b]	376	597, 434[b]
1.8							409	434
1.7					308	487		
1.0	320	393	343	421	308	486	410	434
0.3	319	390	343	421	308	486	410	434

[a] Initial Φ_f for **1**–**4**=0.71, 0.57, 0.21,[4a] and 0.34,[4h] respectively.
[b] Peaks of comparable intensities.

ethynylpyridine systems; no isosbestic points were found, ruling out discrete sequential protonations.[4c] The emission wavelengths are gradually red-shifted, and only the last wavelength shift to the strongest hypsochromic peak at 390 nm involves an isosbestic point. Since the band shape implies a tetraprotonated system, we believe that the most bathochromic emission occurs from a triprotonated state with particularly strong ICT character, and only the transition to the tetraprotonated state involved discrete band-to-band shift with a corresponding iso-emissive point.

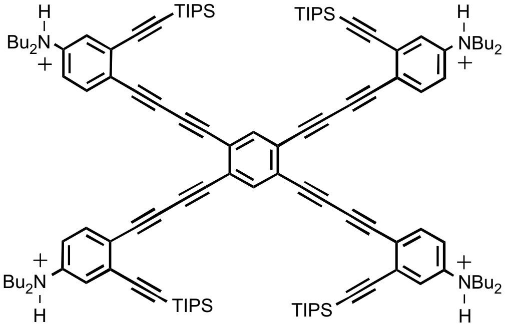
DBA **2** represents a planarized analogue of **1**, with increased vibronic fine structure in the excitation spectra and a lower optical gap due to the enhanced π-overlap of the co-planar system. The emission wavelength is similar to **1**; however, a TFA concentration of $10^{-2.2}$ M is required to generate the most bathochromic emission at 565 nm. This perhaps reflects a decreased basicity due to weak charge transport from the donor nitrogens into the conjugated phenylacetylene network. After this point, the red-shifted band only decreases in intensity as the blue-shifted band at 421 nm is promoted. Due to dual emission from both of these bands at $10^{-2.0}$ M TFA, an interesting pink emission color was observed.

Again, only data points at $10^{-2.2}$ M TFA and greater exhibited an isosbestic point at 524 nm. There is a roughly iso-emissive region about 567 nm for spectra of solutions between 10^{-5} and $10^{-2.6}$ M TFA, but the variation again implies non-distinct dynamic equilibria for mono- and diprotonated states. We do note, however, two overlapping bands at $10^{-3.0}$ M TFA, perhaps reflecting a transition between mono- and diprotonated states.

DBA **3** is an interesting compound for study: it exhibits an unusually sharp and intense low-energy peak in the absorption and excitation spectra as well as two overlapping bands in the emission spectrum (λ_{max}=502 and 541 nm). Since **3** contains a cross-conjugated pathway in the π-system, it is likely that emission from different isolated MO transitions (such as, for instance, a weak charge transfer from the donor groups into the arene core, as mentioned for **2** above) takes place at comparable intensities.[11] Thus, as TFA is added incrementally to solutions of **3**, quenching of emissive intensity is accompanied by promotion of the lower energy emission band with only a slight red shift from 541 to 561 nm, and the fluorescence shifts from green to yellow. Between $10^{-2.3}$ and $10^{-2.1}$ M TFA, a very abrupt change in the emission spectrum occurs, with the generation of a hypsochromically shifted peak at 486 nm at comparable intensity to the peak at 561 nm. If this band corresponds to a $\pi\rightarrow\pi^*$ transition in an electron-poor tetraprotonated state, as it presumably does in **1**, **2**, and **4**, it implies that the nearby (but lower energy) 502 nm band in the neutral state represents emission from localized $\pi\rightarrow\pi^*$ transitions of an electron-rich system, while the 541 nm band represents a delocalized or weak ICT behavior. These very close and overlapping emission bands cover most of the visible region almost equally, and thus the solution at $10^{-2.0}$ M TFA fluoresces nearly pure white. White emission from a single organic fluorophore has been recognized for potential in future display technologies, as issues of differential color aging in OLEDs become more apparent.[12] Further addition of TFA promotes the blue-shifted band. While there are no discernable isosbestic points in the emission spectra, there is one identifiable in the excitation spectra at 525 nm between $10^{-2.1}$ and $10^{-1.0}$ M TFA. It is interesting that the spectrum of tetraprotonated **3** possesses a λ_{max} so close to that of the neutral DBA, and the band shape does not exhibit the same vibronic progression as **1**, **2**, and **4**. The cause of these deviations is not clear, although the unique conjugation pathways in this bis[15]DBA structure likely contribute.

The bis[18]DBA **4** represents the largest system studied here, with diyne linkages connecting the arene rings. It experiences no distortion of the bond angles from linearity and no ring strain. The lowest-energy band in the excitation spectrum is particularly intense, suggesting efficient delocalization along the chromophore pathways. Addition of TFA quenches this band and causes a shift from 553 to 597 nm in the emission, corresponding to a change from bright yellow to dark orange-red. At $10^{-2.0}$ M TFA dual emission is achieved with the appearance of the hypsochromically shifted band at 434 nm, and the solution fluoresces bright purple-pink. It is notable that in this case we actually observe two very close isosbestic points in the emission spectra: at 602 nm between 10^{-5} and $10^{-3.0}$ M TFA, and at 613 nm between $10^{-3.0}$ and $10^{-2.3}$ M TFA (Supplementary data, Fig. S3). This may imply slightly more discrete sequential protonation. Further acid addition suppresses the red-shifted band and promotes the blue band at 434 nm, with an isosbestic point at 556 nm. Note the similar band shape as the bis[14]DBA **2**: one major peak followed by two minor peaks, followed by two shoulders of progressively lower intensity.

To examine the contribution of enforced planarity of the bis[18]DBA system, we also titrated the acyclic precursor to DBA **4** (Supplementary data, Fig. S4). The spectra are very similar to the titration of **4**, but in this case only a 16 nm red shift was observed in the emission, and the most bathochromic maximum at 572 nm was not observed at greater than $10^{-2.4}$ M TFA. The planarity of **4** may lead to a more highly polarized excited state that can emit at longer wavelengths than the acyclic precursor. Unlike **4**, its fully protonated acyclic precursor, dodecayne **5**, emits at a higher relative intensity than the neutral molecule, likely due to the extra electron-donating ability of the TIPS protecting groups. The neutral precursor also possesses a lower fluorescence quantum yield (0.18) than **4** (0.34) in CH$_2$Cl$_2$.[12]



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The stepwise protonation of **1**–**4**, which is accompanied by an emission shifting phenomenon that occurs in different directions in the spectra in two stages, likely reflects the transition of the molecules from electron-rich donor-functionalized systems with $\pi\rightarrow\pi^*$ transitions (or perhaps very weak charge transport from the periphery to the phenylacetylene core) to donor/acceptor-functionalized systems that display strong ICT character. Protonation of all Bu$_2$N groups then converts the compounds to electron-*deficient* systems, again with $\pi\rightarrow\pi^*$ transitions and spectra similar to those observed for non-functionalized analogues with the same carbon skeletons. The very gradual bathochromic shifts in the initial titration spectra imply an interesting ability to fine-tune the degree of charge transfer in the system; ionization of one, two, or three Bu$_2$N groups in a dynamic equilibrium can adjust the emission wavelength over an almost continuous range.

3. Conclusions

The dramatic spectroscopic switching displayed by these compounds is surprising, given the predicted overlapping FMOs. It is likely that partial protonation of the donor groups results in transient donor/acceptor systems with intramolecular charge transfer properties, and modifies the HOMO and LUMO to adopt more spatially separate localizations similar to those calculated in our donor/acceptor-functionalized DBAs and donor/pyridyl-functionalized TPEBs.[4a,c,f–h] The sensitivity of the emission profiles to functional group environment could be exploited potentially for optoelectronic devices or fluorescent sensor arrays.[13] Further structure–properties investigations of these unique organic materials are underway.

4. Experimental section

Compounds **1**–**4** were prepared as previously described.[4a,h] Fluorescence and excitation spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer in four-sided spectrophotometry Quartz cuvettes. Absorption spectra were recorded on an HP 8453 UV/vis spectrophotometer in two- or four-sided spectrophotometry Quartz cuvettes. HPLC/spectroscopy-grade trifluoroacetic acid (Pierce Biotechnology, Inc.) and high-purity spectroscopy-grade CH$_2$Cl$_2$ (Burdick & Jackson, UV λ_{cutoff}=230 nm, deoxygenated) were used without further purification. Solutions of **1**–**4** were prepared for analysis as follows: 0.30 mg of analyte was weighed on a microbalance, dissolved in CH$_2$Cl$_2$, and diluted to a $10^{-3.0}$ M stock solution. A stock solution of $10^{-0.3}$ M TFA was prepared by dissolving 0.372 mL in CH$_2$Cl$_2$ and diluting to 10.0 mL. From this, stock solutions of TFA ranging from $10^{-5.0}$ to $10^{-1.0}$ M were prepared by serial dilutions; 1.0 mL aliquots of each TFA solution were portioned into 2-dram scintillation vials with screw caps, and 20 μL of analyte solution was added to each. The vials were capped, shaken, and the spectra were recorded immediately. Spectra are uncorrected. Excitation and emission slit widths were set to 2.5 and 5.0 nm, respectively, with a PMT voltage of 700.

Acknowledgements

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Supplementary data

Absorption spectra of **1**–**4** titrated with TFA, emission spectra of back-titration of **1**–**4** with *i*-Pr$_2$NH, and absorption, excitation, and emission spectra for TFA titration of acyclic precursor to **4**. This material is available free of charge via the Internet. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.08.059.

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