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Journal Name

ARTICLE

A New Approach to Polycyclic Azaarenes: Visible-light Photolysis of Vinyl Azides in the Synthesis of Diazabenzopyrene and Diazaperylene

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Nitrogen containing polycyclic aromatics are attractive π -functional materials due to their stability and interesting electronic and optical properties. As such, new avenues for the incorporation of nitrogen heteroatoms into arenes are desirable. The visible-light photocyclization of vinyl azides is an efficient method to form nitrogen heterocycles, but previously required complex photocatalyst. Herein we report the cyclization of vinyl azide substituted anthracenes via either thermal activation or visible-light activation without photocatalyst. The result are two novel azaarenes: 1,8-diazabenz[e]pyrene and 3,9-diazaperylene. The electrochemical and photophysical properties of the materials are compared to those of their hydrocarbon analogues. Both materials exhibit increased electron affinities and high quantum yields (up to 82%). Successive protonation of the nitrogen heteroatoms quenches, then fully restores fluorescence at longer wavelengths, indicating these materials are highly sensitive pH sensors.

Introduction

A variety of polycyclic aromatic hydrocarbons (PAHs) have been extensively studied as charge transport materials,¹ light-emitters,² and fluorescent probes.³ Perylene and pyrene derivatives, for example, are used as host and dopant materials in OLEDs,⁴ or as molecular probes.⁵

Replacing CH moieties in PAHs with electronegative nitrogen atoms is an attractive method of manipulating their electronic properties, bestowing n-type charge transport characteristics to typically p-type PAH semiconductors.⁶ The high electronegativity of nitrogen can lower the LUMO energy of polycyclic N-heteroaromatic compounds (N-PAHs) facilitating the injection of electrons and increasing the stability of the resulting radical anion charge carriers. Importantly for charge transport, the introduction of nitrogen into the cyclic framework only causes a small increase in the reorganization energy of the molecule (~ 0.15 eV).⁷ In addition the lone pair of the nitrogen atom adds new functionalities, such as the possibility of hydrogen bonding,⁸ protonation, metal complexation, and may increase solubility.

Though N-PAHs have been known for many years, interest in the electronic and optical properties of these materials is fairly recent.⁹ Nitrogen heteroatoms have been used to tune the electronic properties of graphene,¹⁰ graphene nanoribbons,¹¹ and fullerenes.¹² Among small molecules,

azaarenes are the most common N-PAHs, studied for their n-type or ambipolar charge transport properties.¹³ TIPS-tetraazapentacene, for example, displays impressive electron transport in thin film transistors ($\mu_e = 3.3$ cm²/Vs).¹⁴ Planar triazacoronene was recently synthesized,¹⁵ as well as thiophene fused diazacoronene which was used as an electron donor in conjugated polymers for organic photovoltaics and showed promise as a proton sensor.¹⁶ Heteroacenes containing nitrogen can also act as ion sensors.¹⁷ Like perylene, azaperylenes¹⁸ are strongly fluorescent and are attractive fluorophores for their possible intermolecular interactions or functionalizations, for example, as metal-chelating agents.¹⁹

Despite the interest in extended N-PAHs, recent synthetic approaches are limited and most of them depend on aromatic amines²⁰ as starting materials. Further development of nitrogen-containing materials requires alternative synthetic methods. Vinyl azides, which are formed from aldehydes and therefore easy to introduce onto PAHs, can be used to form a variety of nitrogen heterocycles.²¹ While the photolysis of vinyl azides by UV irradiation has been known since the 1960s,²² only very recent work has focused on visible light activation.²³ The use of low energy visible light reduces photodecomposition processes and requires no specialized equipment. Previous reports have all relied on transition metal photocatalysts, however, increasing the complexity of the reactions.

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[†] Electronic Supplementary Information (ESI) available: Experimental section, NMR spectra, DFT optimized structures and calculated HOMOs and LUMOs, UV-vis spectrum of the photocyclization reaction, concentration dependent PL spectra. See DOI: 10.1039/x0xx00000x

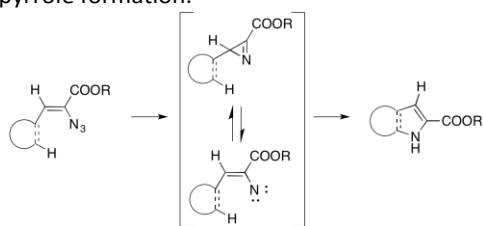
ARTICLE

Here, we report the synthesis of two novel polycyclic N-heteroaromatic isomers, 1,8-diazabenzopyrene **10** and 3,9-diazaperylene **11**. We utilize a Hemetsberger-type reaction in an unprecedented way to fuse pyridine rings to disubstituted anthracene. We found that the regioselectivity of the reaction differs under thermal or catalyst-free photoactivation conditions. The incorporation of nitrogen leads to the stabilization of the frontier orbitals of the compounds and new stimuli-responsive behavior (dual-channel fluorescence sensing of acids) while maintaining the optical band-gap and fluorescent efficiency of the parent compounds.

Results and discussion

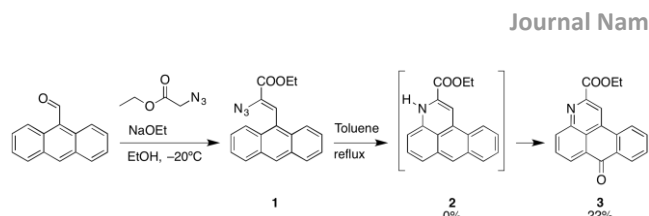
Synthesis

Used in the synthesis of indoles and pyrroles, the Hemetsberger reaction begins with the transformation of a vinyl azide to an azirine intermediate (discernable through IR and NMR measurements and isolable depending on the substituents).^{24,25} The thermolysis of vinyl-2H-azirine produces a vinyl-nitrene intermediate (trappable with triphenylphosphine) that through electrocyclicization and a [1,5]-sigmatropic hydrogen shift forms the desired indole or pyrrole (Scheme 1).²⁶ This method generally produces five-membered rings, though a few examples have shown 6-membered ring formation if an allylic or benzylic carbon is present *ortho* to the vinyl azide.²⁷ We theorized that 6-membered rings could also be achieved on *peri*-substituted PAH where no *ortho*-position is free for pyrrole formation.

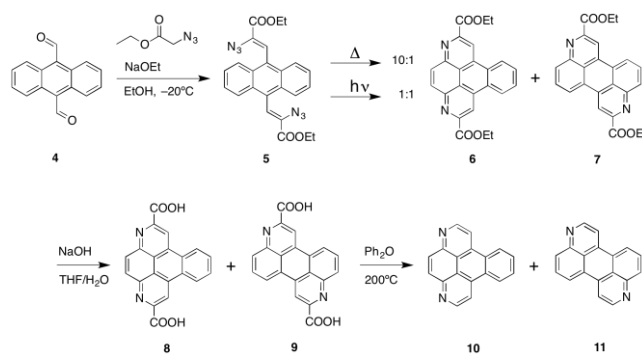


Scheme 1. The Hemetsberger reaction proceeding via azirine and nitrene intermediates.

When Hemetsberger and Knittel first reported their reaction in 1972, they had also explored 6-membered ring formation, but concluded that “an insertion in the *peri*-position could not be achieved if the 2-position was substituted, as in [1-(2-methoxy-naphyl)] and [9-anthryl]. In these cases, only undefined resins occur.”^{26a} As the mechanistic reasons for this failure were not clear, we decided to revisit Hemetsberger’s original reaction with 9-anthryl. The reaction generates several unstable side-products and while the expected product **2** was not isolated, we found that insertion at the *peri*-position does occur, as evidenced by the formation of the oxidized polycyclic compound **3** (Scheme 2). Deducing that fused pyridine **3** could be the product of the spontaneous oxidation of **2** (calculated HOMO = −4.5 eV), we hypothesized that the cyclization of a bis(azidoacrylate) would lead directly to the aromatized diazaarene.



Scheme 2. Synthesis of **3** demonstrating 6-membered ring formation.



Scheme 3. The synthesis of **10** and **11** via thermolysis or photolysis. (Product ratios by ¹HNMR.)

To test this hypothesis, bis(azidoacrylate) precursor **5** was prepared by the base-promoted Knoevenagel condensation of ethyl azidoacetate and 9,10-anthracenedicarbaldehyde **4** (Scheme 3).²⁸ Two cyclization routes could be anticipated for **5**: “*cis*” nitrogen insertion at the 1,4-positions to form diazabenzopyrene **6** or “*trans*” nitrogen insertion at the 1,5-positions to form diazaperylene **7**. Thermolysis of **5** under the classic Hemetsberger conditions (refluxing in toluene) leads predominantly to the formation of **6** (80% isolated yield) with typically less than 10% of **7**. Such selectivity can be rationalized by the electronic effect of the monocyclic intermediate (consider the structure of **2**) that activates the substituted benzene ring towards electrophilic attack, favoring the formation of **6**. It should be noted that the dihydro precursors of **6** and **7** were never observed. Their high HOMO energies (−3.6 eV and −4.1 eV, respectively) suggest that dehydrogenation is spontaneous.

While repeating the cyclization reaction, however, we occasionally noticed higher amounts of **7**. At the same time, we found that yellow solutions of **5** were quickly turning green. An in situ NMR experiment revealed that under visible light at room temperature, **5** undergoes a tandem photocyclization to form both **6** and **7** in a ~1:1 ratio (Scheme 3, Figure 1).²⁹ The photocyclization proceeds consistently and cleanly with no visible side products, though the ratio of **7** (the thermodynamically preferred product by 6.1 Kcal/mol) to **6** increases slightly at lower reaction temperatures (Table S1). At lower temperatures (−10°C and below) we were able to identify an azirine intermediate through its characteristic proton shift at 4.17 ppm (Figure 1 and SI NMR).³⁰ It is known that the extrusion of nitrogen from vinyl azides to form azirines can proceed thermally or photochemically and that azirines themselves are highly photochemically active.^{22,31} Only recently, however, was visible light activation using a ruthenium photocatalyst used to

synthesize pyrroles from vinyl azides.^{23a} In our case, the anthracene core of **5** appears to act as an antenna chromophore, allowing it to react under visible-light without the aid of a photocatalyst. The reaction, which proceeds quickly at room temperature, was also monitored by UV-vis spectroscopy where the appearance of sharp vibronic bands indicated formation of cyclized products (Figure S1). The aforementioned green color of the solutions resulted from a transient band observed at ~600 nm, that is likely attributable to precursors (e.g., H₂-**11** has a predicted HOMO–LUMO gap of 1.9 eV, ~650 nm). A proposed mechanism for the reactions, proceeding via nitrene formation and subsequent insertion into the *peri*-position C–H bond, is shown in Scheme 4.

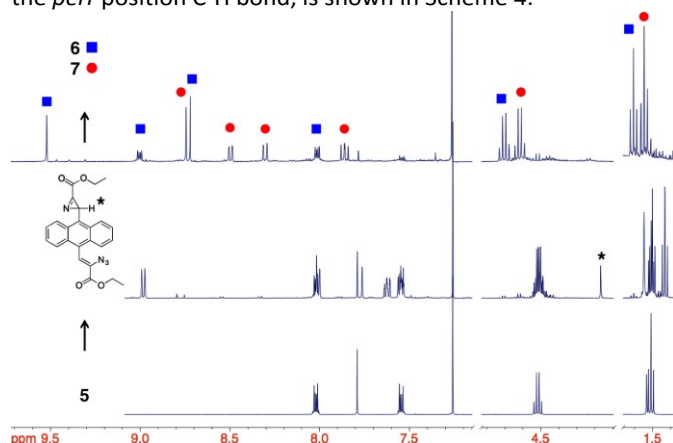
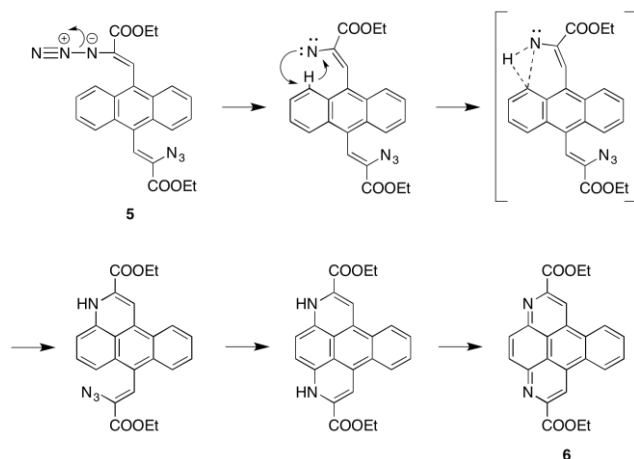


Figure 1. ¹H NMR monitoring of the photocyclization at –50°C in CDCl₃. The bottom spectrum is of the starting vinyl azide **5**. A mixture of **5** and the mono-azirine intermediate is visible in the middle spectrum. The top spectrum shows that the cyclization has completed and a ~1:1 ratio of **6** (■) and **7** (●) is present.



Scheme 4. Proposed mechanism via nitrene C–H insertion.

The ester groups of the above cyclization products were removed by hydrolysis and decarboxylation, affording 95% pure 1,8-diazabenzopyrene **10** in 30% yields from the thermolysis method or a mixture of **10** and 3,9-diazaperylene **11** (23% combined yield) from photolysis (Scheme 3). The pure isomers were then separated by reverse phase column chromatography.

ELECTRONIC PROPERTIES

In order to investigate the effect of nitrogen insertion on the optoelectronic properties of N-PAHs, we performed density functional theory (DFT) calculations and photophysical experiments on **6** (Figure S2-3), **10**, and **11**. Calculations confirmed that the HOMO and LUMO energy levels of **10** and **11** were stabilized by 0.6–0.7 eV compared to their hydrocarbon analogues benzo[e]pyrene and perylene (Table 1), with a slightly stronger stabilizing effect in **10**. The frontier orbitals of **6** and **7** were both further lowered by two ester substituents by ~0.4 eV.

Electrochemical measurements of **10** and **11** showed reversible reduction waves at $E^{1/2} = -2.02$ V and -1.77 V (vs. Fc/Fc⁺), respectively, confirming that the aza-analogues are better electron acceptors than their parent PAHs (Figure 2, Table 1). The values correlate to LUMO levels of -2.78 and -3.03 eV (assuming Fc HOMO at -4.8 eV).

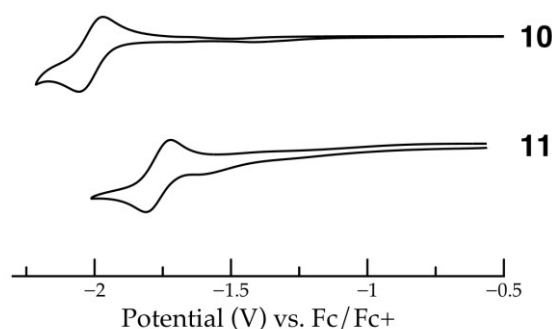


Figure 2. Cyclic voltammetry of **10** (top, MeCN/0.1M TBAPF₆) and **11** (bottom, THF/0.1M TBAPF₆).

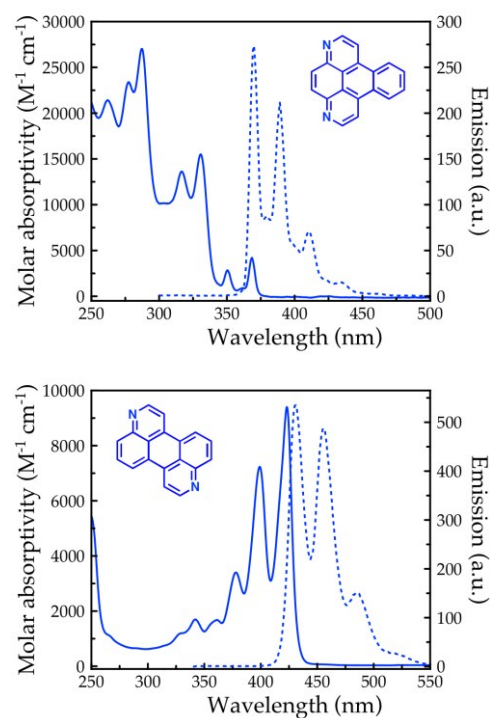


Figure 3. Absorption (—) and emission (---) spectra of **10** (top) and **11** (bottom) in CH₂Cl₂ solutions. ($\lambda_{\text{ex}} = 287$ nm and 330 nm, respectively for **10** and **11**.)

Table 1. Calculated frontier orbitals, HOMO-LUMO gaps,^(a) electrochemical and optical^(b) properties of synthesized N-PAHs and their PAH analogues.

	HOMO (eV)	LUMO (eV)	E_g (eV)	$E_{1/2}^{\text{Red}}$ (V)	LUMO _{CV} (eV)	$\lambda^{\text{abs}}_{\text{max}}$ (nm)	$\lambda^{\text{em}}_{\text{max}}$ (nm)	$\lambda^{\text{em}}_{\text{max}}$ (solid) (nm)	PLQY ^(c)	ϵ (M ⁻¹ cm ⁻¹)
6	-6.57	-2.49	4.08	-1.94	-2.86	285	407		0.03	
10	-6.16	-2.06	4.11	-2.02	-2.78	369	370	474	0.12	4,000
10-2H⁺			3.23			358	459		0.10 ^(d)	
Benzo[e]pyrene	-5.41	-1.39	4.02	-2.60 ³²	-2.20 ³²	340 ³⁴	391 ³⁴	475 ³³	0.04 ³⁴	
7	-6.06	-2.92	3.14							
11	-5.67	-2.49	3.18	-1.77	-3.03	423	431	564	0.82	9,400
11-2H⁺			2.99			451	460		0.78 ^(d)	
Perylene	-4.95	-1.89	3.06	-2.14 ³²	-2.66 ³²	435 ^{(e)36}	436 ^{(e)36}	570 ³⁵	0.94 ^{(e)36}	

(a) DFT calculations at the B3LYP/6-31G(d) level. (b) Measured in CH₂Cl₂ solutions unless noted. (c) Anthracene in ethanol was used as the standard (PLQY = 0.27). (d) Measured in 1% TFA in CH₂Cl₂. (e) Measured in cyclohexane.

The much smaller HOMO-LUMO gap of **11** vs **10** (3.18 eV vs. 4.11 eV) mirrors the differences between their homocyclic analogues, perylene and benzo[e]pyrene (Table 1), and could be rationalized by fewer aromatic Clar's sextets and thus better electron delocalization in **11**. Accordingly, a large red-shift was observed for **11** vs **10** in the UV-vis absorption spectra (Figure 3). Both the absorption and emission bands of **10** and **11** show a pronounced vibronic splitting ($\Delta h\nu \sim 1300 \text{ cm}^{-1}$), indicative of the molecules' rigid π -conjugated structures. **11** emits strongly in solution (photoluminescence quantum yield, PLQY = 0.82 in CH₂Cl₂), while **10** is a weaker emitter (PLQY = 0.12). These values are similar to the quantum yields of their parent PAHs (Table 1) and are in agreement with time-dependent (TD-DFT) calculations that predict a lower transition oscillator strength for **10** (0.12) than for **11** (0.34) (Table S2). Curious to see if **10** or **11** shared pyrene's characteristic excimer formation at high concentration,³⁷ we studied their emission upon addition of water (to induce aggregation) and at increasing concentrations. No sign of excimer formation was observed for **10** (up to 10⁻² M), although new weak emission peaks (430 and 460 nm) become visible for **11** above 10⁻³ M concentrations (Figure S4). In water/MeCN solutions of increasing water content, however, **10** exhibits a continuous enhancement in fluorescence, likely due to its solvent polarity dependent PLQY (Figure S5). The fluorescence of **11** is unaffected, due to its lower polarity, which also causes it to precipitate in water fractions above 60%.

In the solid state, both materials show large red shifts in their excitation and emission spectra (110 nm for **10** and 188 nm for **11**), indicating that fluorescence originates from delocalized excitons (Figure 4). The larger Stokes shift and visibly weaker emission of **11** in the solid state is likely due to higher delocalization/longer diffusion length of its exciton. The observed spectral broadening and disappearance of vibrational structures for both materials resembles the previously reported solid emission behavior of perylene and pyrene.³⁵

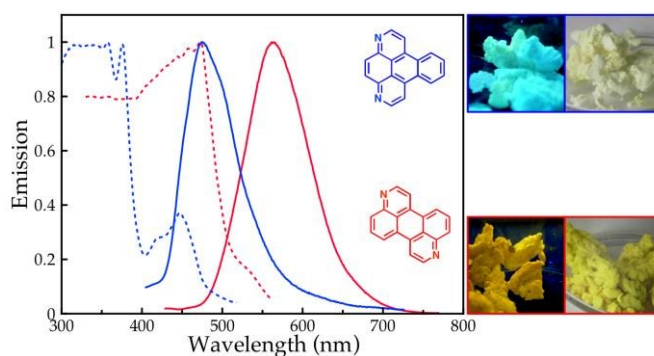


Figure 4. Normalized solid-state emission spectra (—) and excitation (---) spectra of **10** and **11** with images of the polycrystalline materials under UV (left) and natural (right) light. ($\lambda_{\text{ex}} = 380 \text{ nm}$ and 410 nm , $\lambda_{\text{em}} = 550 \text{ nm}$ and 600 nm , respectively for **10** and **11**.)

Due to the presence of basic nitrogen heteroatoms, **10** and **11** undergo pronounced spectroscopic changes when exposed to acids (Figure 5). Titration experiments with trifluoroacetic acid (TFA) reveal a sensitive broadening and red-shift in the absorption spectra of **10** and **11** in MeCN with only 0.01–0.05% TFA. This is accompanied by quenching of fluorescence, attributed to the low emissivity of the mono-protonated species, **10-H⁺** and **11-H⁺**. Continued acidification of the solutions from 0.1% to 1% TFA, however, results in the reappearance of new fluorescent signals, attributed to the diprotonated species **10-2H⁺** and **11-2H⁺**. The emission bands of **10-2H⁺** and **11-2H⁺** are distinctly red-shifted from those of **10** and **11** (by 90 nm and 35 nm respectively), suggesting that these compounds could be useful as dual-band fluorescence pH sensors.³⁸ The comparable quantum yields of the neutral and diprotonated pairs, **10/10-2H⁺** and **11/11-2H⁺**, are especially interesting for the development of ratiometric probes (Table 1). Ratiometric probes are advantageous for fluorescence imaging since the comparison of multiple emission bands provides an internal standard that mitigates the issues of variable instrument parameters, concentration dependence, and photobleaching.³⁹

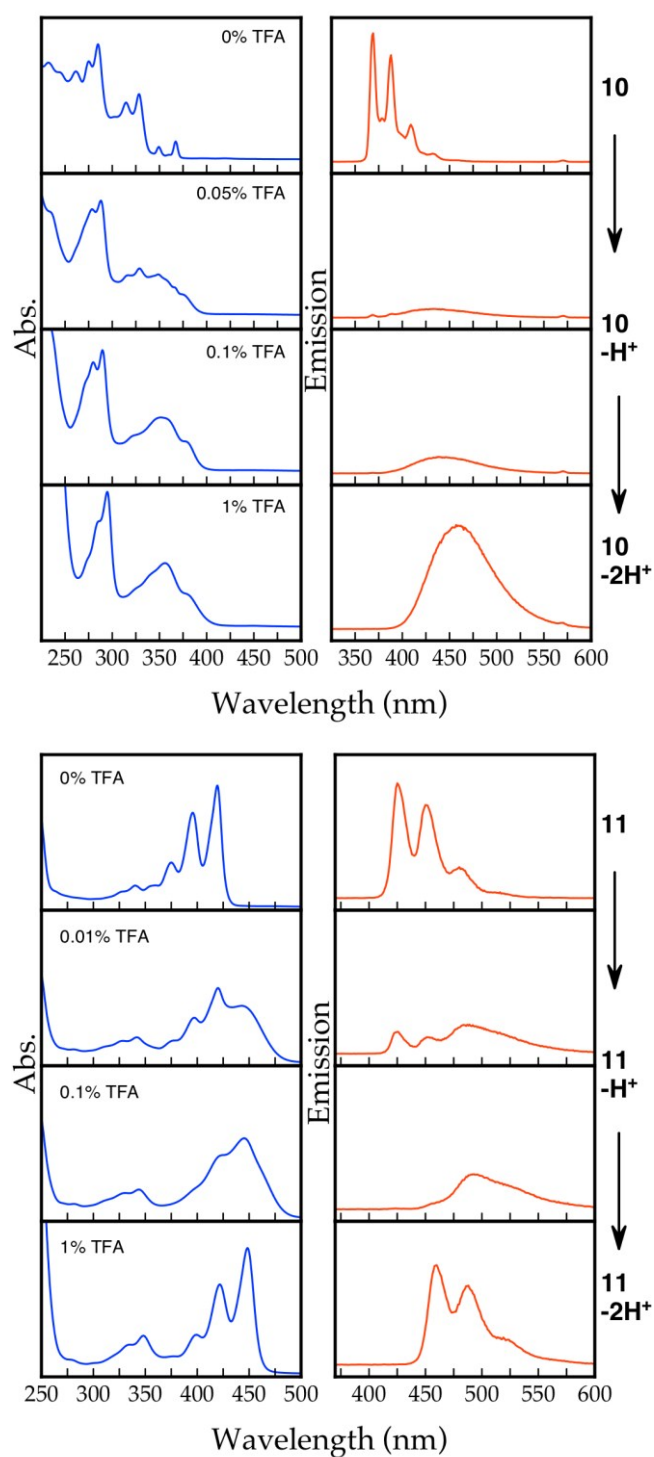


Figure 5. The change in absorption (blue) and emission (red) spectra of **10** (top, 1.1×10^{-5} M) and **11** (bottom, 2.9×10^{-5} M) in MeCN solutions with increasing concentrations of trifluoroacetic acid. ($\lambda_{ex} = 285$ nm and 357 nm, respectively.)

Conclusions

We have demonstrated that vinyl azide derivatives of PAHs with available *peri*-positions can cyclize to form fused pyridine-like structures in near-quantitative yield, representing a new avenue for the synthesis of novel polycyclic N-heteroaromatic compounds. The regioselectivity of tandem cyclizations can be

altered via reaction conditions, as the cyclization can be induced either thermally or photochemically. To our knowledge, the photocyclization of vinyl azide substituted anthracene **5** is the first example of catalyst-free visible light activation of vinyl azides. We have consequently opened new avenues for the synthesis of N-PAHs via visible-light phototransformations starting from readily available PAH-carbaldehydes. The two novel N-PAHs reported herein, 1,8-diazabenzopyrene and 3,9-diazapyrene, have significantly lower HOMO/LUMO levels compared to their parent PAHs and exhibit increased electron affinities. Diazapyrene exhibits better electron delocalization and high quantum yields in solution (82%) compared to diazapyrene (10%). Thus, we have demonstrated that nitrogen heteroatoms can be used to tune the energy levels of known PAH emitters without reducing emission efficiency. N-PAHs also display added functionality, as exemplified by three states of acid-induced fluorescence switching. The documented properties of these molecules have positive implications for their potential use as n-type semiconductors, fluorescent sensors, and light-emitting materials.

Experimental

Synthetic Procedures

Ethyl (Z)-3-(anthracen-9-yl)-2-azidoacrylate (1**)** In a dry 2-neck flask, sodium (0.20 g, 8.7 mmol) was added to dry EtOH (15 mL) under a N_2 atmosphere and the solution was stirred till no sodium remained. In a second dry flask, anthracene-9-carbaldehyde (0.39 g, 1.9 mmol) and ethyl 2-azidoacetate (1.20 g, 9.3 mmol) were combined with dry EtOH (15 mL) and cooled to -20 °C under a N_2 atmosphere. The fresh NaOEt solution was slowly transferred via cannula and the reaction mixture was stirred overnight at -20 °C. The reaction mixture was then poured into saturated $NaHCO_3$ (10 mL) chilled with ice and extracted with ethyl acetate (3×25 mL). The solvent was removed in vacuo and the product purified by column chromatography in 60:40 hexane:chloroform to afford a yellow solid (0.24 g, 40% yield). 1H NMR ($CDCl_3$, 500 MHz, 25 °C) δ 8.51 (s, 1H), 8.07 (d, $J = 7.5$ Hz, 2H), 8.01 (d, $J = 8.5$ Hz, 2H), 7.86 (s, 1H), 7.54 (m, 4H), 4.54 (q, $J = 7.0$ Hz, 2H), 1.53 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, 25 °C) δ 162.7, 131.14, 131.12, 128.97, 128.95, 128.2, 126.9, 125.6, 125.4, 123.8, 62.6, 14.3.

Ethyl 7-oxo-7H-naphtho[1,2,3-de]quinoline-2-carboxylate (3**)** Compound **1** (0.20 g, 0.62 mol) is dissolved in dry toluene (20 mL) and brought to reflux under a N_2 atmosphere. The reaction is monitored by TLC and, when complete, cooled and the solvent is removed in vacuo. The crude product was purified by column chromatography using a gradient of 100% hexane to 40% tetrahydrofuran to afford **3** as a dark solid (0.040 g, 22% yield). 1H NMR ($CDCl_3$, 500 MHz, 25 °C) δ 9.03 (s, 12H), 8.83 (dd, $J = 7.3, 1.3$ Hz, 1H), 8.80 (d, $J = 8.1$ Hz, 1H), 8.57 (dd, $J = 7.8, 1.1$ Hz, 1H), 8.52 (d, $J = 7.9$ Hz, 1H), 8.08 (t, $J = 8.0$ Hz, 1H), 7.84 (td, $J = 7.6, 1.5$ Hz, 1H), 7.76 (td, $J = 7.6, 1.0$ Hz, 1H), 4.68 (q, $J = 7.1$ Hz, 1H), 1.60 (t, $J = 7.1$ Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, 25 °C) δ 182.1, 165.0, 149.1, 146.8, 137.2, 136.8, 134.0, 133.4, 132.2,

131.5, 131.2, 130.8, 128.64, 128.58, 124.4, 124.3, 116.7, 62.8, 14.4. HR-MS (APCI) $m/z = 304.0962$ [M+1] (calcd. for $C_{19}H_{14}NO_3$: $m/z = 304.0968$).

Diethyl 3,3'-(anthracene-9,10-diyl)(2Z,2'Z)-bis(2-azidoacrylate) (5) In a dry 2-neck flask, sodium (2.2 g, 0.095 mol) was added to dry EtOH (100 mL) under a N_2 atmosphere and the solution was stirred till no sodium remained. In a second dry flask, **4** (2.6 g, 0.011 mol) and ethyl azidoacetate (11.4 g, 0.088 mol) were combined with dry EtOH (150 mL) and cooled to $-20^\circ C$ under a N_2 atmosphere. The fresh NaOEt solution was slowly transferred via cannula and the reaction mixture was stirred overnight at $-10^\circ C$. The reaction mixture was then poured into saturated $NaHCO_3$ (20 mL) and ice and let stand in at $6^\circ C$ for 3 hours. The resulting yellow precipitate was collected by filtration and washed with water to afford a bright yellow solid (3.0 g, 59%) The product can be used without further purification or purified by column chromatography using a gradient of 100% hexane to 100% dichloromethane, however solutions of **5** will react if exposed to light. 1H NMR ($CDCl_3$, 500 MHz, $25^\circ C$) δ 8.02 (dd, $J = 6.7, 3.3$ Hz, 4H), 7.79 (s, 2H), 7.55 (dd, $J = 6.8, 3.2$ Hz, 4H), 4.52 (q, $J = 7.2$ Hz, 4H), 1.51 (t, $J = 7.2$ Hz, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz, $25^\circ C$) δ 162.6, 131.5, 128.7, 128.4, 126.2, 126.1, 123.5, 62.7, 14.3. HR-MS (ESI) $m/z = 495.1187$ [M+K] $^+$ (calcd. for $C_{24}H_{20}KN_6O_4$: $m/z = 495.1178$).

Diethyl dibenzo[*f*,*lmn*][2,9]phenanthroline-2,7-dicarboxylate (6) **Thermolysis Method** Compound **5** (0.74 g, 1.6 mmol) is suspended in dry toluene (50 mL) and brought to reflux under a N_2 atmosphere. After refluxing overnight the reaction is cooled and the solvent removed in vacuo. The crude product was purified recrystallization from hot tetrahydrofuran to afford a tan powder of **6** (0.52 g, 80% yield) containing 6% of **7** as an impurity. 1H NMR ($CDCl_3$, 500 MHz, $25^\circ C$) δ 9.56 (s, 2H), 9.03 (dd, $J = 6.1, 3.4$ Hz, 2H), 8.75 (s, 2H), 8.03 (dd, $J = 6.2, 3.3$ Hz, 2H), 4.71 (q, $J = 7.2$ Hz, 4H), 1.61 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (CD_2Cl_2 , 125 MHz, $25^\circ C$) δ 165.4, 148.3, 147.4, 136.92, 133.7, 130.7, 129.5, 124.9, 119.0, 115.6, 62.4, 14.3. HR-MS (ESI) $m/z = 421.1156$ [M+Na] $^+$ (calcd. for $C_{24}H_{18}N_2NaO_4$: $m/z = 421.1159$).

Dibenzo[*f*,*lmn*][2,9]phenanthroline-2,7-dicarboxylic acid (8) NaOH (0.079 g, 2.0 mmol) was added to a suspension of **6** (0.30 g, 0.75 mmol) in a THF/ H_2O (40 mL/10 mL) solution. The reaction is stirred for 2 hrs and then acidified with HCl. The THF is removed in vacuo and the product dissolved in a minimum amount of H_2O . HCl is added to the aqueous solution until no more precipitate is observed. The product is then filtered, washed with H_2O and MeOH, and fully dried to afford a dark brown acid **8** (0.25 g, 98% yield) which was used in the next step without purification. 1H NMR ($(CD_3)_2SO$, 500 MHz, $25^\circ C$) δ 13.64 (s, br, 2H), 9.37 (s, 2H), 9.06 (br, 2H), 8.52 (s, 2H), 7.99 (br, 2H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz, $25^\circ C$) δ 167.0, 148.4, 147.8, 136.6, 133.7, 131.4, 129.2, 125.6, 118.5, 115.7. HR-MS (ESI) $m/z = 343.0717$ [M+] $^+$ (calcd. for $C_{20}H_{11}N_2O_4$: $m/z = 343.0713$).

Dibenzo[*f*,*lmn*][2,9]phenanthroline (1,8-diazabenz[e]pyrene 10) A dry flask was charged with **8** (0.25 g, 0.73 mmol) and

diphenyl ether (20 mL). The flask was evacuated and refilled with N_2 and then brought to reflux for 3.5 hrs. The diphenyl ether is distilled off under vacuum and the resulting solids are sonicated into Et_2O and filtered to afford a yellow powder of **10** (0.060 g, 31% yield) containing 6% of **11** as an impurity. The product was further purified by vacuum sublimation (3.5×10^{-3} mbar) at $140^\circ C$. 1H NMR ($CDCl_3$, 500 MHz, $25^\circ C$) δ 9.39 (d, $J = 5.2$ Hz, 2H), 8.87 (dd, $J = 6.1, 3.3$ Hz, 2H), 8.66 (d, $J = 5.3$ Hz, 2H), 8.56 (s, 2H), 7.93 (dd, $J = 6.2, 3.3$ Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, $25^\circ C$) δ 148.7, 148.2, 135.5, 132.8, 130.0, 129.7, 124.6, 118.2, 114.3. HR-MS (APCI) $m/z = 255.0928$ [M+] $^+$ (calcd. for $C_{18}H_{11}N_2$: $m/z = 255.0917$).

Diethyl dibenzo[*f*,*lmn*][2,9]phenanthroline-2,7-dicarboxylate (6) and **diethyl benzo[1,2,3-de:4,5,6-d'e']diquinoline-2,8-dicarboxylate (7)** **Photolysis Method** Compound **5** (0.30 g, 0.66 mmol) is loaded into a dry reaction vessel under a N_2 atmosphere²⁹ and dry CH_2Cl_2 (100 mL) is syringed in. The reaction is stirred at $-50^\circ C$ under illumination from a 100W compact fluorescent bulb with a 5,000K color temperature. The reaction is monitored by UV-vis and when complete (~ 24 hr) the solvent is removed in vacuo to afford a dark green solid of crude (90% pure) $\sim 1:1$ mixture of **6** and **7** (0.295 g, $>100\%$ yield). The mixture of products was used in the next reaction without purification. 1H NMR ($CDCl_3$, 500 MHz, $25^\circ C$) δ 9.43 (s, 2H), 8.91 (dd, $J = 6.1, 3.4$ Hz, 2H), 8.642 (s, 2H) 8.635 (s, 2H), 8.39 (d, $J = 6.9$ Hz, 2H), 8.22 (d, $J = 8.4$ Hz, 2H), 7.93 (dd, $J = 6.1, 3.3$ Hz, 2H), 7.77 (t, $J = 8.0$ Hz, 2H), 4.63 (q, $J = 7.1$ Hz, 4H), 4.54 (q, $J = 7.1$ Hz, 4H), 1.62 (t, $J = 7.1$ Hz, 6H), 1.57 (t, $J = 7.1$ Hz, 6H).

Dibenzo[*f*,*lmn*][2,9]phenanthroline-2,7-dicarboxylic acid (8) and **benzo[1,2,3-de:4,5,6-d'e']diquinoline-2,8-dicarboxylic acid (9)** were prepared in the same manner as described above for compound **8** in a 70% yield. The mixture of products was used in the next reaction without purification.

Dibenzo[*f*,*lmn*][2,9]phenanthroline (1,8-diazabenz[e]pyrene 10) and **benzo[1,2,3-de:4,5,6-d'e']diquinoline (3,9-diazaperylene 11)** were prepared in the same manner as described above for compound **10** in a 23% yield after sublimation. The two isomers are then separated on a neutral pH C18 reverse phase column from SiliCycle, eluting with a 30% MeCN in H_2O solution containing 0.1% formic acid.

(10) Spectroscopic data is identical to the product prepared (above) by thermolysis method.

(11) 1H NMR ($(CD_3)_2SO$, 500 MHz, $50^\circ C$) δ 8.88 (d, $J = 4.8$ Hz, 2H), 8.55 (d, $J = 7.5$ Hz, 2H), 8.25 (d, $J = 4.8$ Hz, 2H), 7.99 (d, $J = 8.3$ Hz, 2H), 7.81 (t, $J = 7.9$ Hz, 2H). ^{13}C NMR ($(CD_3)_2SO$, 125 MHz, $70^\circ C$) δ 152.1, 149.5, 137.6, 131.6, 130.4, 128.8, 123.6, 123.3, 115.2. HR-MS (ESI) $m/z = 255.0909$ [M+] $^+$ (calcd. for $C_{18}H_{11}N_2$: $m/z = 255.0917$).

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