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Synthesis, Photophysical, Electrochemical, and Halochromic Properties of *peri*-Naphthoindigo

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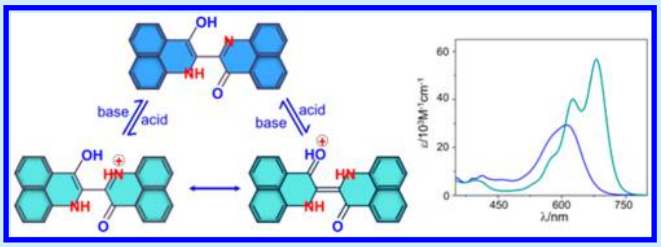
Supporting Information

ABSTRACT: A facile synthesis of *peri*-naphthoindigo (PNI) was reported for the first time from simple precursor. Installation of a chromophore at the *peri*-position of naphthalene is very unique in terms of synthetic challenges and properties. PNI exists in monoenol form, undergoes halochromism in acidic medium, and displays a wide and strong absorption band (ε = 33390 $M^{-1}cm^{-1}$) with maxima at 632 nm (chloroform). The dye undergoes oxidation and reduction at +0.30 and −0.58 V (vs Fc/Fc^{+}), respectively, in chloroform.



peri-Naphthoindigo (PNI), with potential applications in diverse areas, is an organic dye containing cross-conjugated donor−acceptor (H-chromophore) sandwiched between two naphthalene rings through the *peri*-positions (Figure 1). The

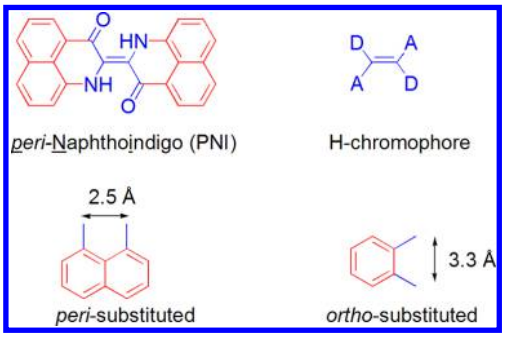


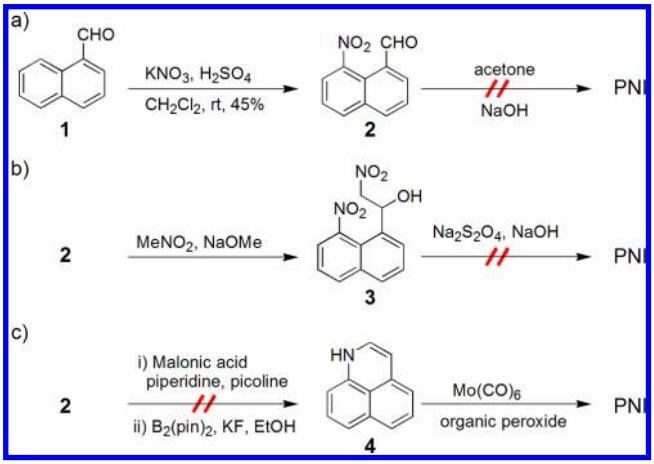
Figure 1. Structure of PNI, H-chromophore, and steric scenarios at the *ortho*- and *peri*-positions.

structure of PNI was proposed for the first time in 1977 by Nathan et al. in a patent claiming it to be a candidate for solar energy applications.[1] A recent theoretical study by Ren and co-workers emphasized PNI as a promising ambipolar organic semiconductor.[2] However, to date, there is no report about the synthesis and properties of this fascinating molecule. On the contrary, analogous compounds with the H-chromophore installed between two *ortho*-substituted benzene rings, namely indigoids, have extensively been studied in the literature. For example, indigo and analogous compounds have been used as vat dye, food colorants, pigments for contact lenses, ambipolar organic semiconductors, and ligands for various metal complexes.[3,4] Thioindigo,[5] *peri*-naphthothioindigo,[6] N,N′-disubstituted indigos,[7] and hemiindigos[8] are known to show photochromic behavior.[9] Hemithioindigos[10] are promising tools in the competitive field of molecular machines.[11]

The unavailability of synthetic methods for PNI can be attributed to different steric scenarios at the *ortho*- vs *peri*-positions. The spatial distance between two *ortho*-protons in an aromatic ring is 3.3 Å, whereas *peri*-protons are separated only by 2.5 Å in naphthalene.[12] Inspired by this fascinating molecule, we accepted the synthetic challenge and herein report for the first time the synthesis, characterization, and photophysical properties of PNI. We have also demonstrated halochromism[13] of the new dye by protonation. Contrary to theoretical predication, PNI exists in monoenol form.

Our pursuit toward PNI was initiated by following Baeyer−Drewsen method for indigo synthesis (Scheme 1a).[14] 1-Naphthaldehyde was nitrated to prepare main precursor **2**,[15]

Scheme 1. Unsuccessful Attempts for the Preparation of PNI



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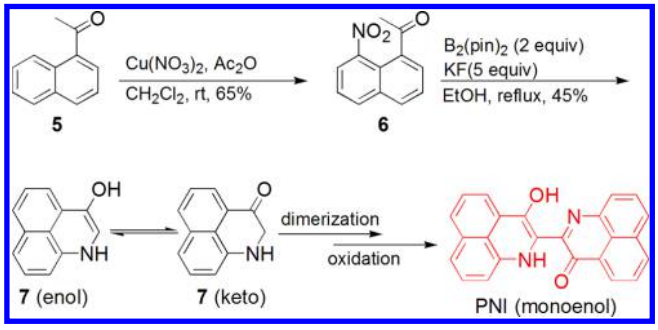
which was treated with acetone in the presence of aqueous NaOH to afford PNI. The cross-aldol reaction and subsequent dimerization process was found to be unsuccessful. Rather, a complicated mixture of multiple compounds was received. Changes in base, temperature, strength of base, and sequence of addition were done to overcome the challenge. However, this did not improve the situation either. All efforts to purify the reaction mixture were found to be fruitless.

The Harley-Mason[16] method was employed in our next attempt to prepare PNI, and the synthetic route is summarized in Scheme 1b. The Henry reaction was carried out by treating **2** with nitromethane in the presence of sodium methoxide. The reaction was found to be ineffective. Different conditions were attempted by changing base and temperature. Despite various modifications, crude yield was limited to 20% only. Isolation of pure product from the nitroaldol reaction was difficult, and the crude mixture containing **3** was treated with alkaline sodium dithionite solution to yield PNI. This synthetic route was also found to be unsuccessful. Our next attempt was to prepare compound **4** and subsequent treatment with $Mo(CO)_6$ and organic peroxide to yield PNI via an oxidative coupling reaction.[17] The synthetic method is described in Scheme 1c. Compound **2** was treated with malonic acid followed by B_2pin_2 in the presence of KF for the preparation of **4**.[18] However, the reaction gave a complex mixture without the desired one.

After exhausting several methods known for the preparation of indigo, we followed a new approach to synthesize PNI. Recently, Song et al.[18] reported that 2-nitrostyrene could be converted into indole by using B_2pin_2 and KF under inert conditions. We anticipated a similar cyclization reaction on the enol form of **6** leading to **7** (Scheme 2). Accordingly, precursor

Scheme 2. Synthetic Route of PNI



6 was prepared following a known method[15b] and refluxed in ethanol in the presence of B_2pin_2 and KF under inert atmosphere (Scheme 2). Instead of the isolation of **7**, a dark greenish-blue color was received after exposing the reaction mixture overnight. The crude mixture was separated by column chromatography and thoroughly characterized by high-resolution mass spectrometry (HRMS), 1D and 2D NMR, and infrared (IR) spectroscopy.

The HRMS spectrum (see Supporting Information) of the dark turquoise solid showed a peak at m/z = 363.1142, which is assigned to protonated PNI. One additional peak was observed at m/z = 347.1179 after fragmentation. The signal is associated with PNI after cleavage of the hydroxy group from the monoenol isomer (Scheme 2). PNI has better solubility in common organic solvent than that of indigo dye. It was indeed possible to record ^1H and ^{13}C NMR in $CDCl_3$. The proton resonance of PNI showed 12 multiplets in the aromatic region along with a sharp singlet at 7.22 ppm and a broad peak at 12.49 ppm (Figure S1). No other peak was noticed in between 0.00 and 13.00 ppm. This can be explained by considering the monoenol form of PNI, in which all aromatic protons are magnetically different. The sharp singlet at 7.22 ppm is assigned to N−H, while a broad peak is attributed to hydroxyl proton. Absence of signal for aliphatic proton established the involvement of methyl group in the reaction via enolization and subsequent conversion into endocyclic double bond. In order to eliminate possibility of merger of any peak with residual chloroform, ^1H NMR was recorded in acetone-d_6 (Figure S2). The spectrum was found to be similar to the one recorded in $CDCl_3$. Connectivity among the multiplets was verified by $^1H-^1H$ correlation spectroscopy (COSY). The COSY spectrum and cross peak correlation among the multiplets is shown in Figure 2. A doublet at 7.16 ppm is

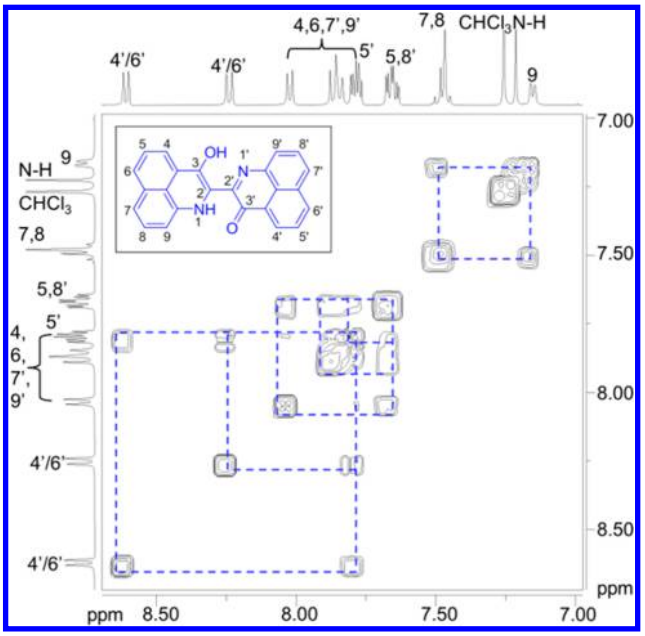


Figure 2. $^1H-^1H$ COSY (400 MHz, 295 K) spectrum of PNI in $CDCl_3$.

assigned to C9-H. The magnetic resonance of C7,8-H was observed together as multiplet at 7.45−7.52 ppm. The low-field doublets at 8.24 and 8.61 ppm are associated with C4′,6′-H. Their correlated cross peak was observed as doublet of doublets (dd) at 7.79 ppm and attributed to C5′-H. Signals for the remaining two benzene rings were observed as four doublets at 7.79, 7.85, 7.87, and 8.03 ppm (4,6,7′,9′-H) and two dd at 7.66 ppm (5,8′-H). Their cross peak correlation was also found to be in agreement with the structure. Further proof of the proposed structure was received from ^{13}C NMR (Figure S4). Twenty-four peaks were observed in between 90.8 and 179.5 ppm. The downfield signal at 179.5 ppm is assigned to the carbonyl group. The presence of the keto group was also confirmed by IR spectroscopy (Figure S9). The stretching vibration of C═O was detected near 1602 cm^{-1}. The broad signal at 3440 cm^{-1} with a shoulder can be associated with the stretching vibration of N−H and O−H. Comparison with the IR frequency of indigo dye (Figure S10) showed a notable difference at around 1172, 1126, 1067, 712, and 563 cm^{-1}, all of which are characteristic of five-membered rings in indigo.[19] Complete disappearance of the peaks around 1126, 712, and

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563 cm^{-1} and very weak signals at around 1172 and 1067 cm^{-1} suggested the absence of a five-membered ring in PNI. A very weak signal at around 1068 cm^{-1} can be attributed to the rocking vibration of C═O. All other signals associated with aromatic C−C, C−H, endocyclic double bond, C−N, and N−H appeared in line with that of indigo dye. To gain insight into the geometry of PNI, solid-state structures would be undoubtedly desirable. Unfortunately, all efforts directed toward the generation of diffractable single crystals proved to be unsuccessful.

The formation of PNI occurred through a series of reaction and was dependent on several factors. Hence, attention was given to various parameters to receive optimum yield. Our initial goal was to carry out cyclization of **6** and isolate **7**. However, under the reaction conditions, **7** underwent dimerization (Figure S8) and subsequent oxidation (possibly during work up) leading to PNI. Such dimerization and oxidation is indeed known in indigo prepration.[20] Since oxidation is an important step in the sequence, we also carried out the reaction under open air atmosphere as well as in pure oxygen. The yield was improved significantly from 21% under N_2 atmosphere to 65% in air. However, the yield was decreased to 12% in pure oxygen. A similar trend was noticed in case of indigo synthesis.[20] We performed the reaction by changing base, solvent and other conditions (Table S1). The best outcome (65%) was achieved when ethanol was used as solvent and KF as base in air. Other bases like NaOH and ^{t}BuOK produced PNI in negligible yield. The aldol reaction was possibly the major reaction in the presence of NaOH. The best result in alcohol can be attributed to stabilization of the enol form of **6**. The other vital step in the synthesis is B_2pin_2-mediated cyclization of **6** to **7**. Different reagents,[21] known for similar cyclization, were employed. However, reaction of **6** with $P(OEt)_3/K_2CO_3$ at 170 ^{o}C did not produce PNI. The reagents and conditions for PNI production were found to be very specific. Treatment of *o*-nitroacetophenone with B_2pin_2 and KF in ethanol did not produce indigo at all. A different steric scenario at the *peri*-position compared to the *ortho*-position was possibly the reason for such an outcome.[12] This also explains our initial failure described in Scheme 1.

Photophysical properties of PNI were investigated and summarized in Table 1. The solution of PNI in chloroform exhibits turquoise color, and the absorption spectrum (Figure 3b) features a broad maximum at around 632 nm with a very strong allowed transition (ε = 33390 M^{-1} cm^{-1}). Compared to indigo, PNI exhibits wider absorption as full width at half maxima of the dye (2964 cm^{-1}) was found to be more than that of indigo (2210 cm^{-1}). Furthermore, the absorption maxima shows bathochromic shift by 29 nm (Table 1). The absorption property of PNI in chloroform remained the same even at various concentrations (1 × 10^{-3} mol L^{-1} to 1 × 10^{-5} mol L^{-1}), ruling out the possibility of any aggregation (Figure S12). Solvent-dependent investigation showed (Figure S11) absorption maxima ranging from 611 nm (MeCN, blue in color) to 632 nm ($CHCl_3$). However, the spectral characteristic remained same, excluding the existence of diketo isomer. Photoluminescence spectrum of PNI in chloroform (Figure S15) showed broad emission with maxima at around 736 nm and Stokes shift of 2235 cm^{-1}, which was found to be longer than that of indigo (1080 cm^{-1}). The relative photoluminescence quantum yield of PNI was measured to be 0.003 in THF. The low quantum yield is common in phenyl analogue compounds.[22]

Table 1. Photophysical Properties of PNI, Indigo, and PNIH$^+$

compd	solvent	λ_{abs} [a] (nm)	λ_{em} [b] (nm)	ε [c] ($M^{-1}cm^{-1}$)
PNI	$CHCl_3$	632	736	33390
PNI	CH_3CN	611	739	29390
indigo	$CHCl_3$	603	645	15940
PNIH$^+$	$CHCl_3$	698		67965
PNIH$^+$	CH_3CN	681		56815

[a]Absorption maxima. [b]Emission maxima. [c]Molar absorption coefficient at experimental λ_{abs}.

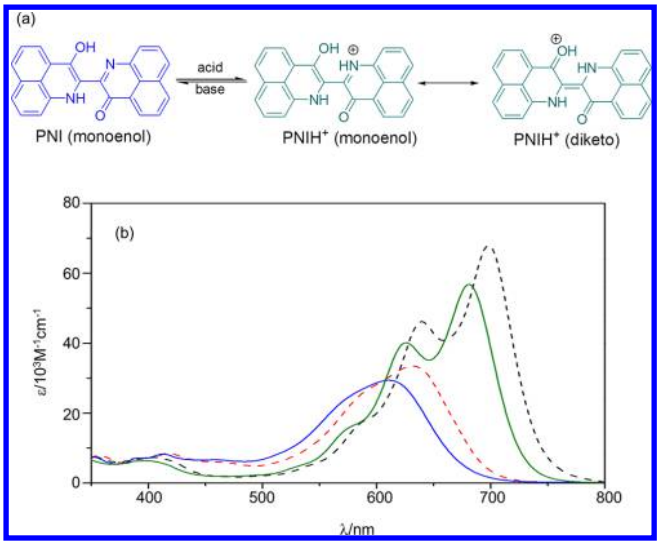

Figure 3. (a) Halochromism of PNI. (b) Absorption spectra (293 K, $c \approx 10^{-5}$ mol L^{-1}) of PNI in chloroform (red, dash), acetonitrile (blue, solid), and PNIH$^+$ in chloroform (black, dash), acetonitrile (olive, solid).

Redox properties of PNI were investigated in chloroform by cyclic voltammetry technique. The dye undergoes oxidation and reduction at +0.30 V and −0.58 V (vs Fc/Fc^+), respectively (Figure S16). The electrochemical features are similar to that one observed for indigo in thin film.[23] However, both redox processes are easier in case of PNI. From the electrochemical data, the energy gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) was measured to be 0.88 eV.

Taking advantage of the structural feature of monoenol PNI, halochromism[13] was installed, and the process was monitored by UV−vis spectroscopy. Upon addition of trifluoroacetic acid to a solution of PNI in chloroform, absorption maxima (Figure 3b, Table 1) shifted bathochromically to 698 nm with an increase in color intensity (ε = 67965 M^{-1} cm^{-1}). Such bathochromic shift associated with protonation is known in indigo[24] and other dyes.[13a] The protonation process is reversible and the initial spectrum can be recovered simply by addition of base (NaOH, NH_4OH). The halochromism process was observed in other solvent (acetonitrile) as well as in the presence of different acids (acetic acid, HCl). Sulfuric acid was avoided as it is known to produce sulfonated product in analogous dye.[24] In acetonitrile, halochromism was visible even in naked eye as color changed from blue to turquoise. The spectroscopic signature (Figure 3b) was similar to that one observed in chloroform. Structure of the protonated dye

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($PNIH^+$) was confirmed by ^1H NMR spectroscopy. Proton resonance of $PNIH^+$ in CD_3CN (Figure S5) displayed three singlet at 6.53, 11.31, and 12.87 ppm (associated with O−H, N−H, and proton at imine nitrogen) along with signals for 12 aromatic hydrogens. The protonated PNI was found to be nonemissive.

In summary, we have successfully reported for the first time the synthesis and characterization of PNI from a simple precursor. A change in the surroundings of the chromophore marks a huge difference in property as well as in synthetic difficulty. The common synthetic methods known for indigo did not work for PNI. On the other hand, indigo cannot be prepared by the method described for PNI. The dye exists in monoenol form, possibly due to better conjugation than the diketo isomer, and has good solubility in common organic solvents. PNI has a strong and wide absorption band. PNI shows halochromism upon protonation. The process is marked by bathochromically shifted maxima (by 66 nm) with an increase in color intensity. Because of the diverse chemistry of naphthalene, PNI will give new dimension to the indigoids' chemistry and the reversible halochromism will contribute significantly to stimuli-responsive molecular switches.[25]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02178.

Synthetic details; NMR, HRMS, IR, absorption, photoluminescence spectra, etc. (PDF)

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Notes

The authors declare no competing financial interest.

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