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Persistent Room-Temperature Radicals from Anionic Naphthalimides: Spin Pairing and Supramolecular Chemistry

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Abstract: *N*-Substituted naphthalimides (NNIs) have been shown to exhibit highly efficient and persistent room-temperature phosphorescence from an NNI-localized triplet excited state, when the *N*-substitution is a sufficiently strong donor and mediates an intramolecular charge-transfer (ICT) state upon photo-excitation. Here we show that when the electron-donating ability of the *N*substitution is further increased in the presence of a carbanion or phenoxide, spontaneous electron transfer (ET) occurs and results in radical anions, verified with electron-paramagnetic resonance (EPR) spectroscopy. However, the EPR-active anion is surprisingly persistent and impervious to nucleophilic and radical reactions under anionic conditions. The stability is thought to originate from an intramolecular spin pairing between the *N*-donor and the NI acceptor post ET, which is demonstrated in supramolecular chemistry.

N-Substituted naphthalimides (NNIs) are a class of electrondeficient aromatic compounds which are extensively exploited as fluorescent sensors (1, Scheme 1)^[1] Recently, we reported a strategy to harvest the triplet excited state of NNIs by introducing a mediating intramolecular charge-transfer state (e.g., 2, replacing N-phenyl with N-methoxyphenyl) to bridge the large energy gap between $\pi^{1}\pi^{-}\pi^{*}$ and $\pi^{-}\pi^{*}$ of the NNI moiety.^[2] As a result, persistent room-temperature phosphorescence (RTP) was obtained and used in low-background imaging. In light of the previous study, one might wonder what happens when the electron-donating ability is further increased, as in the case of carbanion (3) or phenoxide (4) substituted NNI. A plausible process is electron transfer (ET) when the highest occupied molecular orbital (HOMO) of the anion is comparable to or higher than the lowest unoccupied molecular orbital (LUMO) of the NI ring.^[3] It is well known that ET between a donor and acceptor causes the formation of a pair of ionic radicals,^[4] which tend to be unstable and perish overtime.^[5] If made persistent, however, these organic radicals can have important applications such as catalysis, sensing, quantum manipulation, light-emitting and molecular recognition.^[6-16] However, very limited classes of organic radicals are known to exhibit stability against air,[17] especially in the solution state. Here, we report the discovery that N-substituted anionic NIs, such as 3 and 4, show typical radical EPR signals, but are stable against air (up to three years) and chemical reactions as long as their anionic form is maintained, i.e., the organic/aqueous solution or solid is deprotonating enough for the carbanion (3) or phenoxide (4) to exist. Experimental methods including cyclic voltammetry (CV), UV-Vis absorption, luminescence, EPR, and NMR spectroscopy, are used to seek the origin of their persistence. All results point

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Scheme 1. Chemical structures of NNI derivatives 1-4 and their corresponding physical properties depending on the category of donor strength.

to the fact that substantial spin pairing interactions between the anion donor and NI ring may reduce the energy of the open-shell system. Although homodimeric spin-pairing interactions have been routinely used in supramolecular chemistry by Stoddart et al., ^[18] such interactions among heterodimers are rarely explored until recently by Li et al.^[19] Here we show that a polymer gel with an anionic polymeric donor and an NI polymeric acceptor, crosslinked by heterodimeric spin pairing interactions, can be obtained.

The synthesis of NNIs is rather straightforward via a one-step reaction between an amine and 1,8-naphthalic anhydride.^[2] The most striking visual difference for **3** is the indigo color in the solid state and purple in solutions while 1, 2 and the neutral form of 3 (3N) are colorless. While the absorption spectra for 1, 2, and 3N in DMF are almost identical with a major peak at 335 nm, the main absorption band for **3** is dramatically red-shifted to 588 nm, using KOtBu as the deprotonating base due to its reasonable solubility in organic solvent (Figure 1a and Table 1, the study of 4 and derivatives was conducted in aqueous solution and will be presented separately) and the vibrational progressions (ΔE = 1212 cm⁻¹) of **3** indicate a localized π - π * transition instead of an ICT state which is usually structureless. The control anion, deprotonated acetophenone (AP), however, was found to only exhibit a weak, broad shoulder absorption at ~450 nm in the visible region (Figure S1). Interestingly, the absorption of 3 is also much red-shifted compared to that of an N-alky-substituted NI radicals (λ ~420 nm) according to a previous study,^[20] indicating the AP participation. Upon acidification with CF₃COOH, however, the absorption spectrum of 3 reverts back to that of 3N; repeated deprotonation can restore the absorption in the visible region again (Figure S2), indicating full reversibility with pH control. Figure 1b shows the cyclic voltammogram of 1, 2, 3N and 3, where the first three neutral NNIs exhibit reversible reduction at -1.164, -1.171, and -1.163 eV due to the formation of an NNI radical anion; for 3 however, no cathodic or anodic wave could be detected throughout the entire range workable range (Figure S3). The calculated HOMO (~-6.9 eV) and LUMO (~-3.5 eV) energies for 1, 2 and 3N are presented in Table S1, while the values for 3 could not be determined.^[21] However,

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since the measured oxidation potential for **AP**⁻ is -1.340 eV, which translates to a HOMO energy level of -3.35 eV, it can thus be inferred that ET from the **AP**⁻ unit to NI (LUMO ~ -3.5 eV) is a thermodynamically favorable process, according to the Marcus theory on ET.^[22] The lack of reduction peak is understandable given its anionic nature; the fact that a carbanion is resistant to oxidation is quite surprising. Indeed, it was found that typical radical or nucleophilic reactions by an α -carbanion *could not* be achieved by **3**, e.g., for radical polymerization in the presence of various monomers, radical coupling reactions, TEMPO quenching, or Claisen condensitions (Table S2), possibly due to the carbanion's inability to give away electrons when spatially confined to the NI acceptor.



Figure 1. a) Normalized UV-Vis absorption spectra of NNIs **1**, **2**, **3** and **3N** (5 \times 10⁻⁴ M), the neutral form of **3**; b) cyclic voltammograms of these NNIs, (conditions: 5 \times 10⁻⁵ M in DMF; reference electrode, Ag/AgCl; working and auxiliary electrodes, Pt with Bu₄NPF₆; 0.1 M; 298 K; scan rate: 200 mV/s, for **1**, **2**, **3** and **3N**), the CV patterns showing the reversible formation of one single ionic species that correspond to the reduction of the NNIs; for **3**, no reduction or oxidation could be observed.

Table 1. Luminescence properties of 1, 2 ,3N and 3 in DMF at room temperature in air.

compounds	$\lambda_{abs}^{[a]}$ (nm)	$\lambda_{F^{[b]}}$ (nm)	τ ^[c] (ns)	Φ ^[d] (%)
1	335	434	1.52	23.3
2	335	435	1.34	8.5
3N	335	435	2.99	8.4
3	585	682	7.42	0.1

^[a]Maximum absorption wavelength in DMF; ^[b]Fluorescence emission maximum from steady-state spectra (λ_{ex} = 365 nm for **1**, **2**, **3N**; λ_{ex} = 548 nm for **3**); ^[c]Fluorescence lifetime fitted from a single-exponential decay (λ_{ex} = 374 nm for **1**, **2**, **3N**; λ_{ex} = 455 nm for **3**; nanoLED); ^[d] Absolute quantum yield.

In DMF solution, 1 strongly fluoresces in the blue region (λ_{em} = 434 nm) while 2 is more weakly fluorescent (λ_{em} = 435 nm) due to the quenching of a dark ICT state (Figure 2a and Table 1).^[2] The luminescence spectrum of 3 fluoresces in the red region with an emission maximum at 682 nm and a calculated intrinsic lifetime (τ/Φ) of 7.42 µs at room temperature, indicative of a "luminescence" state that has both singlet and triplet characteristics.^[23] This is in huge contrast to 3N, which has essentially the same fluorescence profile as 2. The DMF solutions were then subjected to EPR measurement (Figure 2b); only 3 has signals observable at room temperature even in air. The splitting patterns indicate that the unpaired electrons are in close vicinity of one nitrogen atom and two hydrogen atoms. We suspect that the -CH2 group is in reasonable spatial proximity to the imide N atom to co-influence the unpaired electrons. Figure 2c is the comparison of ¹H-NMR spectra of 3 and 3N, it can be clearly seen that in the presence of a deprotonating base (two NMR peaks at 1.28 and 2.75 ppm corresponding to the t-butanol $-CH_3$ and -OH protons, respectively), the signals are indistinguishable from the baseline, consistent with paramagnetic molecules. Again, upon acidification with CF₃COOH, ¹H-NMR spectrum characteristic of **3N** re-appeared (Figure S4). To eliminate possible ET from the base, we also measured the mixture of 1 and KtOtBu under the same condition and noted no EPR signal (Figure S5); UV-Vis titration may also confirm that adding excess base does not cause spectroscopic change (Figure S6, however, protonation of 3 with acetic acid does cause a complete loss of EPR signal, and repeated deprotonation by adding base can restore the paramagnetic behaviors). The EPR signal of 3 was essentially constant throughout a 90-day period in the presence of excess KOtBu even at 10-3~10-4 M concentrations (Figure S7). In the solid state, however, the sample may be indefinitely stored in a capped vial since the EPR spectrum remains unchanged for three years (Figure S8). It has to be noted that compared to wellknown organic radicals such as TEMPO, the signal of 3 is rather weak since it usually takes sub-mM to obtain decent intensity. Figure 2d shows the results from temperature variable EPR in solid-state DMF (m.p. = 212 K), which do not exhibit any fine structures. Typically, for an intermolecular spin-pairing process, temperatures should favor diamagnetic lower singlet configurations when donor-acceptor distance is reduced. In this case, however, the distance should be constant and this rule may not apply, and the signal increase may be related to reduced quenching at low temperatures. Based on the above spectroscopic results, it is reasonable to believe that the ground state of 3 is a mix of a singlet state and a triplet one, which confer stability and magnetism, respectively (Figure 2e). Following the ET process, the two electrons are still spatially confined to the NNI molecule and are expected to form strong intramolecular spin-pairing interactions which can mitigate the unpaired character, but also reduce their energy.





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exponential lifetime decay of **3**; b) liquid-phase EPR spectrum of **3** in DMF solution (8.9×10^{-3} M) at 273 K; c) ¹H-NMR spectra of **3** (above) and **3N** (below) showing that the anionic form is completely NMR-silent; d) solid-phase EPR spectra of **3** in DMF solution (8.9×10^{-3} M) at 212 K, 180 K, and 140 K; e) schematic illustration of spin-pairing as a result of intramolecular ET from the **AP**⁻ unit to the NI unit, which leads to reduced energy and loss of chemical reactivity in nucleophilic reactions such as the Claisen condensation.

To expand the generality of the anionic system, we also synthesized a series of six NNIs with N-phenoxide donors (Figure 3a and 3b) which are soluble in both DMF and water. As the figure indicates, in aqueous solutions, NNIs 4-6 exhibit EPR signals while 7-9 do not (with 9 showing a slightly distinguishable pattern). Structurally speaking, these two groups do not have dramatic differences. However, their aqueous solutions prepared from reacting with excess KOH did show some visually difference: the first group exhibits a brownish yellow color while the second group is essentially colorless at optically dilute concentrations (Figure S9); as the concentration increases, the first group starts to turn very dark while the second group remains colorless (7 and 8) or turns brownish yellow (9). In Figure 3c, the UV-Vis spectra do seem to show that the absorption of the first group NNIs slightly extends beyond 390 nm. As coloration is an indication for possible charge or electron transfer, it is possible that 4-6 has better HOMO-LUMO energy match than that of 7-9 in water. Again, as long as the pH was deprotonating enough for the N-phenols, the EPR signal was always detectable over a period of 90 days despite that higher concentrations are required vs. detection in DMF. It is possible that the energy of the phenoxide is substantially reduced in highpolarity solvents, so that ET could only happen during a fluctuation in which water molecules adopt a less efficient arrangement for solvation. Nonetheless, the polarity-dependent EPR intensity can be very useful if there NNIs are to be used as molecular probes in polarity or hydrophobicity sensing.

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To demonstrate that the hetero spin-pairing interactions among the AP and the NI ring can be harvested as a driving force for supramolecular chemistry,^[19] we designed a polymer system shown in Figure 4a, where two linear acrylate polymers bear acetophenone and NNI molecules as the side chains, respectively. When an individual polymer was dissolved in DMF in the presence of KOtBu, no conspicuous color or viscosity change could be noted. The electrochemical oxidation or reduction of an individual polymer or mixed one did not yield any observable change as well. Again, the mixed polymers solution was also colorless without adding KOtBu. However, a dark gel immediately formed when the two polymers were mixed in the presence of a deprotonating base (e.g., KOtBu, NaH, LDA, etc., Figure 4b) and strong EPR signal could again be recorded. The variation in EPR pattern between the gel and 3 in DMF could be due to different solvation environments or concentration effects as shown in Figure 4c. We measured the storage modulus (G') and loss modulus (G") of the polymeric gel as a function of angular frequency (ω) (Figure 4d), the frequency sweep plots exhibit an invariance of G' and G'' values over a wide range of ω , and moreover, the values of G' are always higher than those of G", which are characteristics of gels. It has to be noted that the gel starts to liquefy at elevated temperatures and gelates again at lower ones, which indicates that no covalent bonds are formed in the process.

In conclusion, we discovered that spontaneous ET in anionic NNI derivatives can result in persistent radicals at room temperature in organic and aqueous solutions and ascribe the phenomenon to spin-pairing interactions which confer both stability and magnetism. The interactions are explored in supramolecular chemistry to prepare a polymeric gel that is EPR-active and may be useful in applications such as chemochromic magnetic materials.



Figure 3. a)Chemical structures of anionic NNIs that are EPR-active and b) EPR-inactive in aqueous solutions; c) UV-Vis absorption spectra of NNIs **4-9** at 1×10^{-5} M; inset showing varying colors of the NNI aqueous solutions at 1×10^{-3} M; d)-f) liquid-phase EPR spectra of **4-6** in aqueous solutions (8×10⁻³ M) at 298 K.



Figure 4. a) Synthetic procedures of polyacetophenone (**PAP**) and polynaphthalimide (**PNI**); b) pictures showing the mixture of **PAP** and **PNI** at 1:1 ratio (0.1mM) in DMF 0 min (thick liquid, left) and 5 min (gelation, right) after the KOtBu base is added at room temperature in air; c) EPR spectrum of the **PAP/PNI** polymeric gel at room temperature in air from b); d) Oscillation frequency dependency of the storage modulus G' and loss modulus G".

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Conflict of interest

The authors declare no conflict of interest.

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What makes an anion stable and exhibit radical characters? When it is spatially confined to an electron deficient aromatic molecule, a carbanion or phenoxide becomes a persistent radical-like species at room temperature, presumably due to spinpairing interactions. Interesting supramolecular chemistry may thus be constructed.



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