Photoexcited Naphthalene Diimide Radical Anion Linking the Nodes of a Metal−Organic Framework: A Heterogeneous Super-reductant

Subhadip Goswami,[†,#] Jordan N. Nelson,[†,#] Timur Islamoglu,[†] Yi-Lin Wu,[*,†,§,∥] Omar K. Farha,[*,†,‡,∥] and Michael R. Wasielewski[*,†,§,∥]

[†]Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States

[§]Argonne−Northwestern Solar Energy Research (ANSER) Center, Northwestern University, Evanston, Illinois 60208, United States

[∥]Institute for Sustainability and Energy at Northwestern (ISEN), Northwestern University, Evanston, Illinois 60208, United States

[‡]Department of Chemistry, Faculty of Science, King Abdulaziz University, Jeddah 22254, Saudi Arabia

Aromatic organic anions are reactive species involved in various chemical transformations.[1−4] The photochemistry and photophysics of these species have been the subject of extensive study as they have been implicated in many photoinduced electron transfer processes, and are demonstrated to be powerful reducing agents.[5−11] Such properties were substantiated by the observation of rapid electron ejection to give solvated electrons, electron−cation pairs, or reduced electron acceptors upon photolysis of aromatic anions (e.g., sodium pyrenide or biphenylide).[5,7] Though most of the strongly photoreducing chromophores absorb in the UV or the blue part of the solar spectrum, aromatic anions tend to display absorption in the visible and near-infrared region, suggesting their potential for reductive artificial photosynthesis.

In particular, the naphthalene-1,8:4,5-bis(dicarboximide) radical anion ($NDI^{\bullet-}$, $E_{NDI(0)/NDI(1-)}$ ~ −0.5 V vs saturated calomel electrode, SCE) is electrochemically stable[12,13] and absorbs from 400 to 800 nm, with absorption maxima at 470, 610, 700, and 780 nm.[14] These properties suggest that the photoexcited state of $NDI^{\bullet-}$ should be a more powerful photoreductant with $E_{NDI(0)/NDI(*,1-)}$ ~ −2.1 V, than the UV-absorbing [tris(2,2′-phenylpyridine)]iridium (fac-Ir(ppy)$_3$, $E_{(+)/(*,0)}$ ~ −1.7 V),[15] even reaching to the potential needed for energy-demanding direct CO_2 reduction ($CO_2 + e^- \rightarrow [CO_2]^{\bullet-}$, E = −2.14 V).[16] $NDI^{\bullet-}$ can be easily generated by electrochemical methods,[14] mild reductants such as cobalto-cene ($CoCp_2$) or tetrakis(dimethylamino)ethylene (TDAE),[17,18] or photoreduction of neutral NDI by alkyl-amines[19] as the result of its low reduction potential. Efficient photoinduced electron transfer from the excited $*NDI^{\bullet-}$ to Re-based CO_2-reducing catalysts has been reported in covalent molecular dyads/triads, illustrating the potential of $*NDI^{\bullet-}$ as an electron donor for solar fuels generation.[18,20−22]

Recently, there has been growing interest in electrochemically active metal−organic frameworks (MOFs).[23] The high porosity of these materials imparts facile mass transport and ion conductivity, and the crystallinity ensures homogeneous chemical reactivity across the solids. Indeed, electrochromic behavior has been reported for NDI- and pyrene-based MOFs with fast color switching rates, and the donor−acceptor interactions between π-acidic NDI and electron rich molecules have been utilized to sense organic guests.[24−33] The combination of powerful organic photoreductants and MOF architecture is thus anticipated to provide an opportunity for reductive chemical transformations. Specifically, we report here the synthesis and characterization of an UiO-type MOF (UiO-NDI, Figure 1) composed of Zr_6-based metal node and linearly disubstituted N,N-bis(2,6-dimethyl-4-benzoic acid)-NDI (NDI-COOH).[34] The Zr(IV) oxide-based structure was selected for its high chemical stability[35] and the meta-dimethyl groups in the NDI unit provide solubility for the MOF synthesis. The strong photoreducing power of the reduced MOF, UiO-$NDI^{\bullet-}$, is tested against the reduction of chlorocarbon derivatives, a class of common pollutants resistant to reductive chemistry.

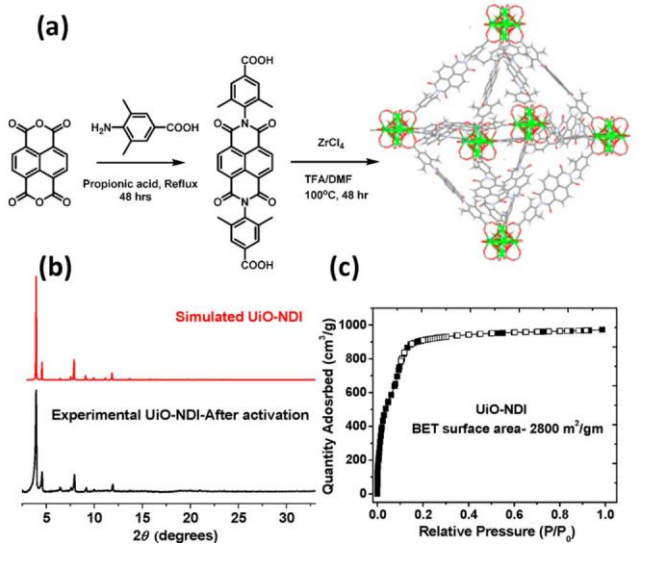


Figure 1. (a) Synthesis of UiO-NDI and the schematic representation of the octahedron cage in the MOF. Color code used for the Zr_6O_8 node cluster: Zr = green, O = red. (b) Comparison between the powder X-ray diffraction pattern of UiO-NDI, red = simulated, black = synthesized and after activation. (c) Nitrogen adsorption (■) and desorption (□) isotherms measured at 77 K, BET area is given.

The formation of UiO-NDI MOF makes use of solvothermal synthesis in N,N-dimethylformamide (DMF) at 100 °C in the presence of trifluoroacetic acid as the modulator, NDI-COOH as the ligand, and $ZrCl_4$ as the metal source. The resultant octahedral crystals (~0.5 μm, Figure S2) exhibit powder X-ray diffraction patterns consistent with the predicted structures of the fcu-topology, the most common topology observed with ditopic linkers and Zr_6-based nodes (Figure 1b). The permanent porosity were supported by N_2 isotherm measurement at 77 K after supercritical CO_2 activation followed by heating at 120 °C under vacuum for 12 h; a type IV reversible isotherm with Brunauer−Emmett−Teller (BET) surface area of 2800 $m^2\ g^{-1}$ was observed (Figure 1c).

The UV−vis spectrum of the suspension of UiO-NDI in DMF indicates the absorption <400 nm predominant from NDI (Figure 2a). It is important to note that the vibronic

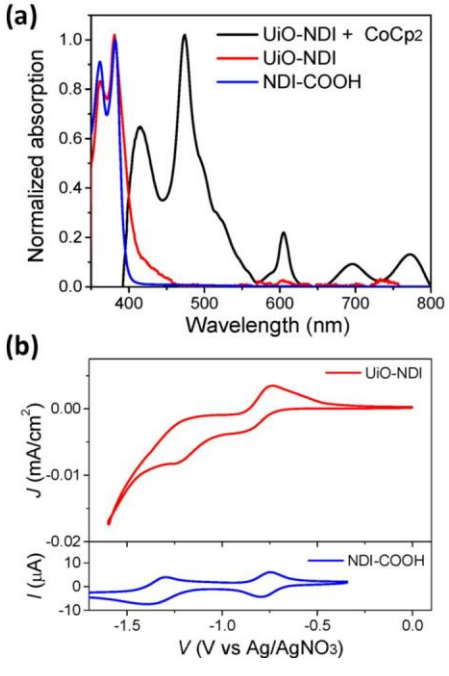


Figure 2. (a) UV−vis absorption spectra of the NDI ligand (blue line), UiO-NDI (red), and UiO-$NDI^{\bullet-}$ (black) generated by cobaltocene ($CoCp_2$). (b) Cyclic voltammograms of UiO-NDI measured in the solution of 1 M nBu_4NPF_6 in CH_2Cl_2 (red line) and the NDI linker (1 mM) in the solution of 0.1 M nBu_4NPF_6 in DMF (blue).

progression (0-0 band around 380 nm and 0-1 band around 360 nm) commonly observed for monomeric NDI derivatives is well resolved, indicative of minimal electronic coupling between neighboring NDIs. Such an observation is consistent with the long centroid-to-centroid distance of 13.6 Å between NDIs according to the structural model. Similarly, when the suspension of UiO-NDI was reduced by $CoCp_2$, monomer-like UV−vis absorption of NDI radical anions was observed. The electrochemical behavior of UiO-NDI was examined by cyclic voltammetry; the samples were prepared by electrophoretic deposition (EPD) on fluorine-doped tin oxide (FTO) substrates from suspended MOF samples in toluene. Once again, the typical monomer-like, two one-electron reduction waves of NDI were observed (Figure 2b). These observations are significant in that incorporation of redox active sites within MOF structures preserves the electronic properties of the individual chromophore, and the otherwise energy-dissipating H-/J-aggregate or excimer formation is prohibited. The combination of UV−vis and electrochemical data suggest that the −2.1 V vs SCE photoreducing power is maintained in UiO-$NDI^{\bullet-}$.

Figure 3 summarizes the results of electron paramagnetic resonance (EPR) spectroscopy used to probe the spin

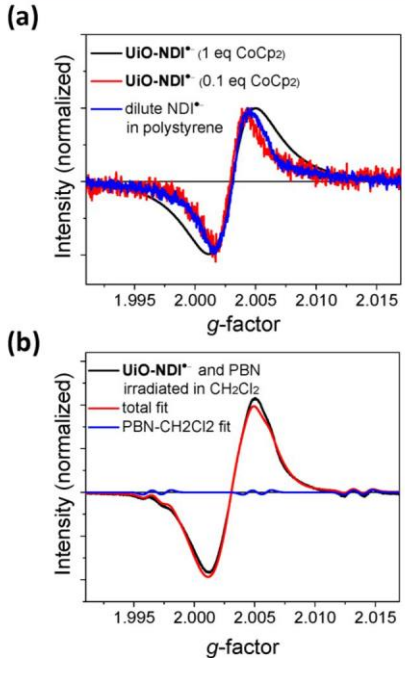


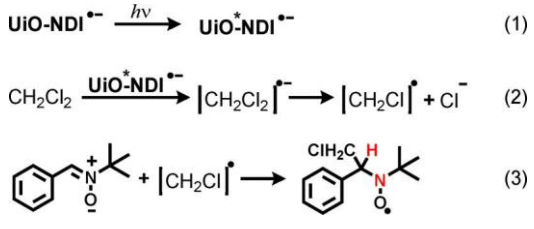
Figure 3. (a) CW-EPR spectra of $NDI^{\bullet-}$ diluted in a polystyrene matrix and UiO-NDI chemically reduced with 1 and 0.1 equiv $CoCp_2$. (b) CW-EPR spectra of reduced UiO-NDI (1 equiv $CoCp_2$) soaked in CH_2Cl_2 illuminated with 480 nm light (15 mW average power) for 2 h in the presence of N-tert-butyl-α-phenylnitrone (PBN) spin trap. The total fit (two components) of the spectrum is shown along with the minor component attributed to the PBN spin adduct.

distribution of the reduced UiO-$NDI^{\bullet-}$ MOF. The singly reduced NDI radical anion was generated with $CoCp_2$ in a minimal amount of CH_2Cl_2. The broad radical signal in the continuous-wave (CW) EPR spectrum is the result of $NDI^{\bullet-}$ in a randomly oriented solid state, as would be expected from the UiO-NDI crystalline powders. To test the possibility of electron-hopping between the NDI units in the MOF,[36−38] varying equivalents of $CoCp_2$ were investigated, but the CW-EPR spectra of UiO-$NDI^{\bullet-}$ remain essentially unchanged. The slightly larger width for fully reduced UiO-$NDI^{\bullet-}$ is likely due to a general increase in spin density, resulting a reduction of transverse relaxation lifetime (T_2) and, inversely, an increase in line width.[39] A significant decrease in the spectral width of UiO-$NDI^{\bullet-}$ at lower concentrations of $NDI^{\bullet-}$ (fewer equivalents of $CoCp_2$) was not observed, concluding the radical is not delocalized between NDI units on the EPR time scale. Instead, the spectrum of UiO-$NDI^{\bullet-}$ in the latter case remains comparable to that of dilute $NDI^{\bullet-}$ in polystyrene. Additionally, no wide-field spectra were observed in any case, precluding the influence of Zr nuclei on $NDI^{\bullet-}$. This result indicates that the electronic behavior of $NDI^{\bullet-}$ as a linker in the MOF is comparable to that of isolated $NDI^{\bullet-}$. The excited $NDI^{\bullet-}$ in the MOF structure is therefore unlikely to be quenched by interactions between neutral and reduced NDI.

With the properties of the neutral and reduced forms of UiO-NDI characterized, its photochemical reactivity was tested by attempting to reduce CH_2Cl_2. Such a solvent was chosen as the target not only because of its conventional use in dissolving and delivering $CoCp_2$ for UiO-NDI$^{\bullet-}$ generation, but it also represents one of the most difficult pollutant substrates to be removed by reductive degradation.[40,41] Whereas the reduction potential of chlorinated hydrocarbons often exhibits some degree of electrode-dependence,[40,42,43] the reduction on-set was measured to be −2.0 V vs SCE on a glassy carbon electrode (Figure S3),[40,44] and most highly chlorinated aliphatic or aromatic hydrocarbons exhibit milder reduction potentials.

To monitor the photoreduction process, samples of UiO-NDI$^{\bullet-}$ were irradiated with 480 nm light in the presence of CH_2Cl_2 and N-tert-butyl-α-phenylnitrone (PBN). The latter compound is known to react with short-lived and reactive radical species ("spin trapping") by forming a longer-lived spin adduct with the radical as described in Scheme 1. The

Scheme 1. Mechanism of CH_2Cl_2 Reduction by Photoexcited UiO-NDI$^{\bullet-}$ Radical Anions and N-tert-butyl-α-phenylnitrone (PBN)-Spin Adduct Formation[a]



[a]Hyperfine-contributing nuclei of primary interest are highlighted in red.

characteristic electron−nuclear hyperfine coupling constants of the nitroxide nitrogen and benzyl hydrogen in the radical spin adduct can be used to identify the radical that has been generated and trapped.[45] Upon irradiation at 200 K, a new set of EPR radical signal is observed on top of the central feature of UiO-NDI$^{\bullet-}$ (most noticeable at g ~ 1.995 and 2.015, Figure 3b). This radical has the splitting pattern indicative of principally one N and one H hyperfine interaction, as is expected from a PBN spin adduct. The temperature of 200 K was selected to maximize the lifetime of the transient radical, but remain well above of the freezing point of CH_2Cl_2; the analogous experiment performed in frozen CH_2Cl_2 at 85 K did not yield spin-trap signals, implying a diffusion-limited reaction.

Though the central portion of the feature attributed to the spin adduct overlaps with that of UiO-NDI$^{\bullet-}$, the distortion of the derivative shape of the main signal is clearly visible, and the fit to the feature attributed to the spin adduct alone is shown in Figure 3b. Previous cathodic electrochemical investigations of chlorinated aliphatic hydrocarbons have suggested that the reduction should result in the two-step or concerted liberation of mineralized Cl^- ions and a carbon-based free radical (Scheme 1, eq 2).[40,41] The observed spin-trap product shows hyperfine constants (a_N = 1.45 mT and a_H = 0.27 mT) that are in a good agreement with that of the reported PBN spin adduct of the $^{\bullet}CH_2Cl$ radical (a_N = 1.429 mT and a_H = 0.291 mT) generated in CH_2Cl_2 by photolysis of an azido-Pd(II) complex.[46] In comparison, the formation of this radical adduct was not observed from 480 nm photoexcitation of PBN on its own in CH_2Cl_2 or of the sample containing both UiO-NDI$^{\bullet-}$ and PBN in tetrahydrofuran (THF) in place of CH_2Cl_2. When UiO-NDI$^{\bullet-}$ was irradiated in CH_2Cl_2 in the absence of PBN, no spectral change was observed after exposure to light at 298, 200, or 85 K. When a solution of the reduced NDI ligand and PBN in CH_2Cl_2 were irradiated at 480 nm, the radical adduct was not observed, either (Figure S4).

The weak spin-adduct EPR signal compared to that of UiO-NDI$^{\bullet-}$ could be due in part to the transient nature of the $^{\bullet}CH_2Cl$ radical and, perhaps more importantly, to the short photoexcited state lifetime of *NDI$^{\bullet-}$ (140 ps)[14] that competes inefficiently with diffusional intermolecular electron-transfer reactions. The intermolecular electron-transfer rate may be enhanced by the use of a cationic redox mediator[47,48] by virtue of favorable Coulombic interactions. Nevertheless, the detection of the $^{\bullet}CH_2Cl$ radical is strong evidence for the potential of the UiO-NDI$^{\bullet-}$ MOF for carrying out energy-demanding reduction processes. The absence of spin-adduct formation by the *[NDI-COOH]$^{\bullet-}$ ligand in CH_2Cl_2, likely due to intermolecular deactivation, shows the advantage of UiO-NDI MOF as a super-reductant.

In summary, we have demonstrated that a crystalline and porous Zr(IV)-based UiO-NDI MOF scaffold can be utilized to incorporate strongly photoreducing chromophores. The wide spacing between chromophores and the weak electronic coupling through space or the Zr_6 nodes prevent deactivation of the excited state and thus preserve the monomer-like photochemical reactivity. The strong photoreducing power of UiO-NDI$^{\bullet-}$ was evidenced by the reductive degradation of CH_2Cl_2. This work also suggests that a promising catalytic photoreduction scheme can be envisaged by rapid electrochemical regeneration of UiO-NDI$^{\bullet-}$ on FTO.[24,27]

■ ASSOCIATED CONTENT

* Supporting Information

Instrumental techniques, synthesis, PXRD and pore size distributions, SEM images, electrophoretic depositions of UiO-NDI films, electrochemistry of CH_2Cl_2, and addi-tional EPR spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*yi-lin.wu@northwestern.edu (Y.-L.W.).

*o-farha@northwestern.edu (O.K.F.).

*m-wasielewski@northwestern.edu (M.R.W.).

ORCID

Subhadip Goswami: 0000-0002-8462-9054

Timur Islamoglu: 0000-0003-3688-9158

Yi-Lin Wu: 0000-0003-0253-1625

Omar K. Farha: 0000-0002-9904-9845

Michael R. Wasielewski: 0000-0003-2920-5440

Author Contributions

#S.G. and J.N.N. contributed equally.

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Notes

The authors declare no competing financial interest.

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