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Article

Syntheses, Structures, and Photochemistry of Manganese Nitrosyls Derived from Designed Schiff Base Ligands: Potential NO Donors That Can Be Activated by Near-Infrared Light

C. Gianna Hoffman-Luca, Aura A. Eroy-Reveles, Jose Alvarenga, and Pradip K. Mascharak*

Department of Chemistry and Biochemistry, University of California, Santa Cruz, California 95064

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Two manganese nitrosyls, namely, $[Mn(SBPy_3)(NO)](ClO_4)_2$ (**1**) and $[Mn(SBPy_2Q)(NO)](ClO_4)_2$ (**2**), have been synthesized by using designed pentadentate Schiff base ligands *N*,*N*-bis(2-pyridylmethyl)amine-*N*-ethyl-2-pyridine-2-aldimine ($SBPy_3$) and *N*,*N*-bis(2-pyridyl methyl)amine-*N*-ethyl-2-quinoline-2-aldimine ($SBPy_2Q$). Reaction of NO(g) with $[Mn(SBPy_3)(MeOH)](ClO_4)_2$ and $[Mn(SBPy_2Q)(EtOH)](ClO_4)_2$ in MeCN affords **1** and **2**, respectively, in good yields. Narrow-width peaks in the ^1H NMR spectra and strong ν_{NO} at 1773 cm^{-1} (of **1**) and 1759 cm^{-1} (of **2**) confirm a strongly coupled {low-spin Mn(II)-NO•}formulation for both these $\{Mn\text{-}NO\}^6$ nitrosyls. In MeCN, **1** exhibits two strong absorption bands with λ_{max} at 500 and 720 nm. These bands red shift to 550 and 785 nm in case of **2** because of substitution of the pyridyl-imine moiety of $SBPy_3$ with quinolyl-imine moiety in the $SBPy_2Q$ ligand frame. Exposure of solutions **1** and **2** to near-infrared (NIR) light (780 nm, 5 mW) results in rapid bleaching of the orange and fuchsia solutions, and free NO is detected in the solutions by an NO-sensitive electrode. The high quantum yield values (Φ) of **1** (0.580 ± 0.010, λ_{irr} = 550 nm, MeCN) and **2** (0.434 ± 0.010, λ_{irr} = 550 nm, MeCN) and in particular their sensitivity to NIR light of 800−950 nm range strongly suggest that these designed manganese nitrosyls could be used as NIR light-triggered NO donors.

Introduction

During the past three decades, nitric oxide (NO) has been shown to participate in a number of biological functions including blood pressure regulation, neurotransmission, cell-mediated immune response, and antimicrobial activity.[1] This diatomic gaseous molecule is produced endogenously by the enzyme NO synthase (NOS), which catalyzes the oxidation of L-arginine to L-citrulline.[2] NO is highly soluble in lipid bilayer, a fact that allows for its simple diffusion across cell membranes. In most regulatory processes, relatively low concentrations (nM) of NO are required.[3] Quite in contrast, elevated levels (μM) of NO triggers apoptosis (programmed cell death). Selective delivery of high concentrations of NO to cancerous cells could therefore result in tumor suppression.[4]

The discovery of the regulatory roles of NO in a myriad of biological processes has prompted synthetic chemists to design and isolate compounds that can deliver NO to cellular targets. Exogenous NO donors that have so far been synthesized and employed include organic nitrates and nitrites, nitrosothiols, and diazeniumdiolates (NONOates).[5−8] For example, nitroglycerine and sodium nitroprusside (SNP) have been used to combat hypertensive episodes for quite sometime.[9] Most of the NO donors are activated by various stimuli

*To whom correspondence should be addressed. E-mail: pradip@chemistry.ucsc.edu.

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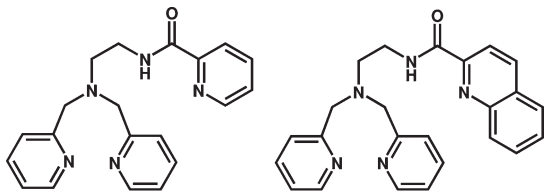
such as heat, light, change in pH, or metabolic activation.[10] Inorganic metal NO complexes (nitrosyls) such as SNP[9] and Roussin's salts[11] have been shown to release NO upon exposure to UV light (340−440 nm). Such UV-driven NO delivery is, however, detrimental to human tissue because of both exposure to UV light and harmful effects of ancillary ligands (such as CN^-) or iron-containing intermediates.[12] These problems along with low quantum yield values (Φ) limit the use of these iron nitrosyls as light-triggered NO donors.[13]

Systemic NO drugs such as organic nitrites and nitrosothiols are hardly suitable for delivering high doses of NO to hypoxic malignant locales because of severe hypotensive (and other toxic) effects elsewhere in the body.[14] NO donors that release NO upon exposure to illumination therefore warrant more attention since NO delivery by compounds of this type could be conveniently controlled via selected exposure of the targeted area to light. Such compounds could be employed in Photodynamic Therapy (PDT) of certain types of cancers.[15] In PDT of skin cancers, it is necessary to employ NO donors that are sensitive to near-infrared (NIR) light since light penetration through mammalian tissue is mainly limited to 700−1100 nm region.[16] It is, however, important to note that wavelengths longer than 800 nm are rarely used for PDT because of high scattering in tissue.[17] Hence, compounds that absorb in the 700 to 800 nm range are highly desirable. Metal nitrosyls that can rapidly release NO under NIR light definitely belong to this type of compounds and are potential candidates for PDT.

As part of our drug design research, we have been involved for some time in the isolation of designed metal (M = Fe,[18−20] Ru,[21−24] Mn[25−29]) nitrosyls that release NO upon exposure to low-intensity (mW to W) light of different wavelengths (300−650 nm). The first example of such species is the $\{Fe\text{-}NO\}^6$ nitrosyl[30] $[Fe(PaPy_3)(NO)](ClO_4)_2$ derived from the designed pentadentate ligand *N,N*-bis(2-pyridylmethyl)-amine-*N*-ethyl-2-pyridine-2-carboxamide ($PaPy_3H$; H is the dissociable carboxamide H).[18] This diamagnetic non-heme nitrosyl rapidly releases NO upon illumination with 5−10 mW of visible light (500−600 nm) in solvents such as acetonitrile (Φ = 0.18).[20] The corresponding $\{Ru\text{-}NO\}^6$ nitrosyl $[Ru(PaPy_3)(NO)](BF_4)_2$ exhibits NO photolability under UV illumination.[21] We have also synthesized a series of $\{Ru\text{-}NO\}^6$ nitrosyls coordinated to tetradentate planar dicarboxamide N_4 ligands that also release NO upon exposure to light in the range 320−500 nm.[22,23] In this series of nitrosyls, replacement of pyridine group(s) with quinoline moieties (more conjugation in the ligand frame) shifts the λ_{max} of the nitrosyls from ∼350 nm to ∼500 nm. The $PaPy_3H$ ligand was therefore modified to incorporate a quinoline group to generate the pentadentate ligand *N,N*-bis(2-pyridylmethyl)-amine-*N*-ethyl-2-quinoline-2-carboxamide, ($PaPy_2QH$, where the H is a dissociable proton). Indeed, the $[Ru(PaPy_2Q)(NO)](BF_4)_2$ complex proved to be a more efficient NO delivering agent (λ_{max} = 420, Φ_{410} = 0.17) compared to $[Ru(PaPy_3)(NO)](BF_4)_2$ (λ_{max} = 410 nm, Φ_{410} = 0.05).[24] It is therefore evident that the coordinated quinoline moiety increases the photoactivity. Both these ruthenium NO donors have been used to deliver NO to biological targets, such as myoglobin and cytochrome c oxidase.[21,25] Unlike the $\{Fe\text{-}NO\}^6$ nitrosyls, most of the $\{Ru\text{-}NO\}^6$ nitrosyls we have synthesized are stable in water (pH 7).[21] However, most of them exhibit NO photolability when exposed to light of wavelengths below 500 nm.



$PaPy_3H$ **$PaPy_2QH$**

To synthesize metal nitrosyls that are sensitive to visible or NIR light, we looked into manganese NO complexes. Although organometallic compounds,[31] porphyrin[32] and

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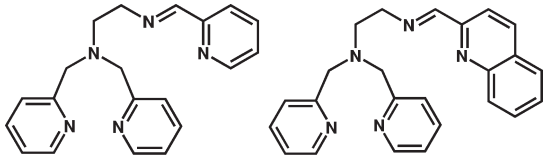
phthalocyanine[33] complexes containing Mn−NO linkage have been reported, very few mononuclear coordination complexes of manganese with bound NO have been reported. In our early work, we reported the first $\{Mn\text{-}NO\}^6$ complex, namely, $[Mn(PaPy_3)(NO)](ClO_4)$, that releases NO when exposed to visible light (500−650 nm). This green nitrosyl with λ_{max} = 635 nm transfers NO to enzymes such as papain,[27] cytochrome c oxidase,[25] and soluble guanylate cyclase.[34] Interestingly, $[Mn(PaPy_2Q)(NO)](ClO_4)$, a nitrosyl with a quinoline moiety (λ_{max} at 670 nm), exhibits significant NO photolability upon exposure to visible light of lower energy (650−750 nm range).[29] Both these nitrosyls have been incorporated into sol−gel matrixes and employed to transfer NO to myoglobin.[29]

One structural feature that is consistent in all of our designed photoactive $\{M\text{-}NO\}^6$ (M = Fe, Ru, Mn) nitrosyls is the presence of one (or two) coordinated carboxamido-N donor(s) around the metal center. To determine whether the presence of such a donor is required for the observed NO photolability, we have recently designed a similar ligand (*N*, *N*-bis(2-pyridylmethyl)amine-*N*-ethyl-2-pyridine-2-aldimine, $SBPy_3$) that contains an imine N instead of a carboxamido-N.[35] Surprisingly, the iron complex of this designed ligand, namely, $[Fe(SBPy_3)(DMF)](ClO_4)_3$, does not react with NO.[35] In addition, this Fe(III) complex is very unstable and spontaneously reduced to the corresponding Fe(II) species $[Fe(SBPy_3)(MeCN)](ClO_4)_2$ when dissolved in MeCN. We therefore undertook the task of synthesizing the $\{Mn\text{-}NO\}^6$ nitrosyl derived from $SBPy_3$ starting from Mn(II) salts. In such attempts, the quinoline-substituted ligand *N,N*-bis(2-pyridylmethyl)amine-*N*-ethyl-2-quinoline-2-aldimine ($SBPy_2Q$) was also included. In this account, we report the syntheses, structures, and spectroscopic properties of two nitrosyls $[Mn(SBPy_3)(NO)](ClO_4)_2$ (**1**) and $[Mn(SBPy_2Q)(NO)](ClO_4)_2$ (**2**). Both nitrosyls are extremely sensitive to light. Most importantly, these two nitrosyls release NO rapidly upon exposure to low-intensity (mW) visible and NIR light (500−950 nm). The unusual sensitivity to NIR light of these two $\{Mn\text{-}NO\}^6$ nitrosyls has been studied and compared with the photochemical parameters of $[Mn(PaPy_3)(NO)](ClO_4)$ (**3**) and $[Mn(PaPy_2Q)(NO)](ClO_4)$ (**4**). The results are also discussed in this paper.



$SBPy_3$ $SBPy_2Q$

Experimental Section

Quinoline-2-carboxaldehyde and Mn(II) perchlorate hexahydrate were purchased from Alfa Aesar and used without further purification. Acetonitrile (MeCN), ethanol (EtOH), methanol (MeOH), and diethyl ether (Et_2O) were obtained from Fisher Chemical Co. and distilled from CaH_2, $Mg(OEt)_2$, $Mg(OMe)_2$, and sodium/benzophenone, respectively, prior to use. Nitric oxide gas was purchased from Spectra Gases and purified from higher oxides by passage through a KOH column before use in reactions.

Caution! *Transition metal perchlorates should be handled with great caution and be prepared in small quantities as metal perchlorates are hazardous and may explode upon heating.*

Synthesis of the Compounds. The ligands *N,N*-bis(2-pyridylmethyl)amine-*N*-ethyl-2-pyridine-2-carboxamide ($PaPy_3H$),[19b] *N,N*-bis(2-pyridylmethyl)amine-*N*-ethyl-2-quinoline-carboxamide ($PaPy_2QH$),[29] and *N,N*-bis(2-pyridylmethyl)amine-*N*-ethyl-2-pyridine-2-aldimine ($SBPy_3$)[35] were synthesized according to the literature procedures. The starting materials (2-aminoethyl)bis(2-pyridylmethyl)amine (DPEA)[36] and $[Mn(SBPy_3)Cl]ClO_4$ (**5**)[28] were also synthesized according to the literature procedures.

***N,N*-Bis(2-pyridylmethyl)amine-*N*-ethyl-2-quinoline-2-aldimine ($SBPy_2Q$).** A solution of 0.230 g (1.48 mmol) of 2-quinolinecarboxaldehyde in 5 mL of MeOH was added slowly to a solution of 0.450 g (1.85 mmol) of DPEA in 15 mL of MeOH, and the reaction mixture was heated to reflux under dinitrogen for 5 h. Next, the solvent was removed completely under vacuum, and the brown oil was redissolved in 125 mL of methylene chloride (DCM). The solution was then washed several times with distilled water, and the DCM layer was dried with anhydrous $MgSO_4$. Removal of DCM afforded pure $SBPy_2Q$ as dark red oil (0.45 g, 80% yield). Selected IR frequencies (cm^{-1}, KBr disk): 3388 (m), 1645 (m, ν_{CN}), 1591 (s), 1433 (s), 755 (s). ^1H NMR (500 MHz, CD_3CN, δ from TMS): 8.53 (t, 1H), 8.32 (d, 1H), 8.28 (d, 1H), 8.21 (d, 1H), 8.12 (m, 1H), 8.05 (d, 1H), 7.92 (d, 1H), 7.85 (t, 2H), 7.76 (t, 2H), 7.59 (m, 2H), 7.12 (t, 2H), 4.00 (s, 4H), 3.96 (t, 2H), 3.05 (t, 2H).

$[Mn(SBPy_3)(NO)](ClO_4)_2$ (1). A batch of 100 mg (0.19 mmol) of $[Mn(SBPy_3)Cl]ClO_4$ (**5**) was dissolved in 10 mL of MeOH and thoroughly degassed. Next a batch of 94 mg (0.21 mmol) of $AgClO_4$ was dissolved in 3 mL of MeOH and added to the yellow-orange solution of the manganese complex while stirring. After 2 h, the reaction mixture containing a white precipitate was filtered through a Celite pad, and the solvent was removed in vacuo. The yellow oil was then redissolved in MeCN and thoroughly degassed. The Schlenk flask was wrapped in Al foil, and NO gas was bubbled through the solution for 20 min. The yellow orange solution was then stored under NO atmosphere for 48 h while stirring at room temperature. Slow diffusion of Et_2O into the MeCN solution of the resulting nitrosyl afforded dark red crystals (0.80 mg, 80% yield). Anal. Calcd for $[Mn(SBPy_3)(NO)](ClO_4)_2$ (**1**, $C_{20}H_{21}N_6Cl_2O_9Mn$): C, 39.04; H, 3.44; N, 13.66. Found: C, 39.01; H, 3.42; N, 13.72. Selected IR frequencies (cm^{-1}, KBr disk): 1773 (s, ν_{NO}), 1611 (w), 1467 (w), 1090 (vs, ν_{ClO4}), 769 (m), 622 (m). Electronic absorption spectrum in MeCN (prepared in the dark), λ_{max} (nm) (ε (M^{-1} cm^{-1})): 340 (1725), 500 (1990), 720 (750). Electronic absorption spectrum in H_2O (prepared in the dark), λ_{max} (nm) (ε (M^{-1} cm^{-1})): 345 (1605), 500 (1820), 720 (720). ^1H NMR (500 MHz, CD_3CN, δ from TMS): 9.27 (d, 1H), 9.12 (s, 1H), 8.31 (d, 1H), 8.16 (t, 1H), 7.95 (t, 2H), 7.73 (t, 1H), 7.53 (d, 2H), 7.22 (t, 2H), 6.54 (d, 2H), 4.71 (d, 2H), 4.45 (d, 2H), 4.29 (t, 2H), 3.60 (t, 2H).

$[Mn(SBPy_2Q)(EtOH)](ClO_4)_2$ (6). To a solution of 120 mg (0.31 mmol) of $SBPy_2Q$ in 15 mL of degassed EtOH was added a batch of 113 mg (0.31 mmol) of solid $Mn(ClO_4)_2 \cdot 6H_2O$, and the mixture was stirred overnight. The solvent was removed in vacuo, and the pale brown solid thus obtained was washed several times with Et_2O and then dried under vacuum

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Table 1. Summary of Crystal Data, Intensity Collection, and Structural Refinement Parameters for $[Mn(SBPy_3)(NO)](ClO_4)_2$ (**1**) and $[Mn(SBPy_2Q)(NO)](ClO_4)_2$ ($\mathbf{2}\cdot CH_3CN$)

	1	$\mathbf{2}\cdot CH_3CN$
formula	$C_{20}H_{21}Cl_2MnN_6O_9$	$C_{26}H_{26}Cl_2MnN_7O_9$
molecular weight	615.27	706.38
cryst color, habit	orange-brown rod	magenta shard
T, K	150(2)	150(2)
cryst syst	orthorhombic	triclinic
space group	$Pca2_1$	$P\bar{1}$
a, Å	13.334(11)	9.817(10)
b, Å	12.518(11)	12.365(13)
c, Å	14.805(13)	12.595(13)
α, Å	90	95.351(2)
β, Å	90	96.736(10)
γ, Å	90	99.306(2)
V, Å^3	2471.4(4)	1488.5(3)
Z	4	2
d_{cald}, g cm^{-3}	1.654	1.576
abs coeff, mm^{-1}	0.814	0.688
GOF[a] on F^2	1.052	1.014
R1[b] %	0.0528	0.0565
wR2[c] %	0.1499	0.1320

[a] GOF = $[\sum[w(F_o^2 - F_c^2)^2]/(M-N)]^{1/2}$ (M = number of reflections, N = number of parameters refined). [b] R1 = $\sum||F_o| - |F_c||/\sum|F_o|$. [c] wR2 = $[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $[Mn(SBPy_3)(NO)](ClO_4)_2$ (**1**) and $[Mn(SBPy_2Q)(NO)](ClO_4)_2$ (**2**)

	1	**2**
Mn−N1	2.007(4)	2.025(4)
Mn−N2	1.985(4)	2.092(3)
Mn−N3	2.028(4)	2.026(3)
Mn−N4	2.014(4)	2.019(4)
Mn−N5	1.999(4)	1.979(4)
Mn−N6	1.649(4)	1.651(4)
N6−O1	1.167(6)	1.179(4)
Mn−N6−O1	177.2(4)	175.3(3)
N6−Mn−N5	92.14(19)	91.22(16)
N5−Mn−N4	163.38(16)	162.86(14)
N5−Mn−N1	97.09(15)	99.48(14)
N6−Mn−N3	102.00(18)	95.91(15)
N4−Mn−N3	82.88(17)	80.62(15)
N6−Mn−N2	175.81(19)	173.52(16)
N4−Mn−N2	85.99(16)	92.12(15)
N3−Mn−N2	82.04(17)	81.63(14)
N6−Mn−N4	93.36(19)	93.39(16)
N6−Mn−N1	97.48(18)	104.92(15)
N4−Mn−N1	97.72(16)	95.26(14)
N5−Mn−N3	80.64(17)	82.44(15)
N1−Mn−N3	160.45(16)	159.00(14)
N5−Mn−N2	89.61(16)	82.53(14)
N1−Mn−N2	78.52(16)	77.93(14)

(174 mg, 83% yield). Selected IR frequencies (cm^{-1}, KBr disk): 3391 (s), 1604 (s), 1440 (m), 1090 (vs, ν_{ClO4}), 761 (m), 626 (s). μ_{eff} (298 K, polycryst) = 5.85 μ_B.

[Mn(SBPy$_2$Q)(NO)](ClO$_4$)$_2$ (2). A batch of **6** (0.200 g, 0.29 mmol) was dissolved in 15 mL of MeCN and thoroughly degassed. The Schlenk flask was then wrapped in Al foil, and NO gas was passed through the solution for 10 min. The fuchsia solution thus formed was stirred under NO pressure for 24 h at room temperature. Finally, 30 mL of degassed Et_2O was added via cannula, and the solution was stored in the dark at −20 °C for 72 h. The fuchsia crystals that separated during this period were collected by filtration, washed with Et_2O, and dried in vacuo (0.80 g, 38% yield). Anal. Calcd for $[Mn(SBPy_2Q)(NO)](ClO_4)_2\cdot$MeCN (**2**·MeCN) $C_{26}H_{26}N_7Cl_2O_9Mn$: C, 44.08; H, 3.98; N, 13.84. Found: C, 44.10; H, 3.87; N, 13.78. Selected IR frequencies (cm^{-1}, KBr disk): 3428 (m), 1759 (s, ν_{NO}), 1610 (m), 1454 (m), 1087 (vs, ν_{ClO4}), 793 (m), 623 (m). Electronic absorption spectrum in MeCN (prepared in the dark), λ_{max} (nm) (ε (M^{-1} cm^{-1})): 330 (12 850), 550 (2100), 785 (1200). ^{1}H NMR (500 MHz, CD_3CN, δ from TMS): 9.47 (s, 1H), 9.26 (d, 1H), 8.73 (d, 1H), 8.35 (d, 1H), 8.23 (d, 1H), 8.17 (t, 1H), 7.95 (m, 3H), 7.53 (d, 2H), 7.10 (t, 2H), 6.42 (d, 2H), 4.63 (d, 2H), 4.53 (d, 2H), 4.34 (t, 2H), 3.48 (t, 2H).

X-ray Data Collection and Structure Solution and Refinement. Diffraction data for single crystal of **1** and **2**·MeCN were collected at 150 K on a Bruker APEX-II diffractometer. Mo Kα (0.717073 Å) radiation was used, and the data was corrected for absorption effects. The structures were solved by direct methods (SHELXS-97). All nonhydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were added geometrically and refined with the use of a riding model. Machine parameter, crystal data, and data collection parameters for complexes **1** and **2** are summarized in Table 1, while selected bond distances and angles are listed in Table 2. Complete crystallographic data for $[Mn(SBPy_3)(NO)](ClO_4)_2$ (**1**) and $[Mn(SBPy_2Q)(NO)](ClO_4)_2\cdot CH_3CN$ ($\mathbf{2}\cdot CH_3CN$) have been submitted as Supporting Information.

Physical Measurements. ^{1}H NMR spectra were recorded on a Bruker 500 MHz spectrometer at 298 K. Absorption spectra were recorded on a Cary 50 Varian spectrophotometer. A Perkin-Elmer 1600 FT-IR spectrometer was used to acquire infrared spectra. Room temperature magnetic susceptibility measurements were performed with a Johnson-Matthey magnetic susceptibility balance. Real-time detection of NO in solution under aerobic conditions was monitored with an *in*NO Nitric Oxide Measuring System (Innovative Instruments, Inc.) using an *ami*NO-2000 electrode.

Photochemical Experiments. Continuous-wave photolysis studies were performed using a Newport Oriel Apex Illuminator (150 W xenon lamp) equipped with an Oriel 1/8 m Cornerstone Monochromator. The intensity of light was checked prior to each experiment with a Coherent Field Max II-T0 Laser Power Meter. Known concentrations of the samples were prepared under dim light and protected from extraneous light. All irradiations were performed under aerated conditions and all samples were placed in a 10 × 4 mm quartz cuvette. To avoid interference from higher energy light, measurements at NIR region were performed with cutoff filters; this ensured correct wavelength selection in our measurements.

The rates of NO release were measured by recording the electronic spectrum of **1**, **2**, **3**, and **4** in MeCN (1 mM, 0.6 mL) and monitoring the loss of absorbance at an appropriate wavelength of samples exposed by monochromatic light (of selected wavelengths, power range 1.0−3.0 mW) for defined intervals. Observed rate constant values k_{NO} were obtained by fitting the kinetic traces to the equation $C(t) = C_\infty + (C_0 - C_\infty)\{\exp(-k_{NO}t)\}$, where C_0 and C_∞ are the initial and final concentration values at fixed wavelength, respectively. The apparent rate constant values of NO loss (k_{NO}) were then calculated from the ln(C) versus time plot of the various NO donors. Quantum yield (Φ) measurements were performed by standard actinometry using Reinecke's salt to calibrate the light source at 500 and 550 nm.[37] A 1 mM solution of **1** and **2** was prepared and placed in 10 × 4 mm quartz cuvette. The absorbance along the 10 mm path was greater than 2.0 at the desired wavelength, ensuring that >99% of the incident light was absorbed. The sample was irradiated with monochromatic light (>2 mW) for defined time intervals. The photolysis was monitored by recording the electronic absorbance along the 4 mm path of the cuvette at an appropriate wavelength for maximal change in the absorption spectrum. For example, aqueous solutions of **1** were monitored at 720 nm. Because the

(37) Wegner, E. E.; Adamson, A. W. *J. Am. Chem. Soc.* **1966**, *88*, 394.

photoproduct does not exhibit any absorption in the visible region, complete loss of absorption at both 500 and 720 nm was taken as the end point of the photolysis (100% conversion to photoproduct) for complex **1**. Since the concentrations of NO in the light-exposed solutions of the nitrosyls are proportional to the time of exposure (vide infra), in the following discussions, it is assumed that the quantum yield values do reflect the efficiency of NO generation by these nitrosyls upon illumination.

Results and Discussion

Syntheses. Previously, we reported the syntheses of $[Mn(PaPy_3)(NO)](ClO_4)$ (**3**) and $[Mn(PaPy_2Q)(NO)](ClO_4)$ (**4**), two photoactive manganese nitrosyls derived from ligands with carboxamide groups, namely, $PaPy_3H$ and $PaPy_2QH$.[29] The spectroscopic parameters of these two $\{Mn\text{-}NO\}^6$ nitrosyls indicated that addition of conjugated ring systems to such ligand frames shifts the position of the photoband of the resulting nitrosyls to lower-energy region. To determine the role of the carboxamido-N donor in the observed NO photolability of **3** and **4**, we have now synthesized the corresponding Schiff base ligands $SBPy_3$ and $SBPy_2Q$. These two ligands have been synthesized in ~80% yields by coupling DPEA with pyridine-2-carboxaldehyde and 2-quinolinecarboxaldehyde respectively in anhydrous MeOH.

In our earlier attempts, the high spin Mn(II) complex $[Mn(SBPy_3)Cl]ClO_4$ (**5**, μ_{eff} = 5.90 μ_B) did not directly react with NO gas to afford any $\{Mn\text{-}NO\}^6$ nitrosyl.[28] We suspected that the low affinity of NO toward Mn(II) center could be responsible for this failure. Therefore, in the present work, we have first removed the Cl^- from the coordination sphere by reacting **5** with $AgClO_4$ in degassed MeOH to generate the purported solvato species $[Mn(SBPy_3)(MeOH)]^{2+}$. Filtration of the reaction mixture through a Celite pad (to remove AgCl) and removal of the solvent affords $[Mn(SBPy_3)(MeOH)](ClO_4)_2$ as a yellow oil. Reaction of NO with this Mn(II) solvato species in MeCN slowly turns the solution dark burgundy over 24 h, yielding the nitrosyl $[Mn(SBPy_3)(NO)](ClO_4)_2$ (**1**). Diffusion of diethyl ether into this solution affords crystals of **1** in high yield (80%). Nitrosyl **2** has been synthesized from the Mn(II) complex $[Mn(SBPy_2Q)(EtOH)](ClO_4)_2$ (**6**), which is isolated as a pale brown solid from the reaction of $Mn(ClO_4)_2\cdot 6H_2O$ and $SBPy_2Q$ in EtOH. Complex **6** contains a high-spin Mn(II) center (μ_{eff} = 5.85 μ_B) much like **5**. When a solution of **6** in degassed MeCN is exposed to NO gas, the color changes to a clear dark fuchsia solution (over 72 h) from **2** and can be isolated in moderate yield (~40%). It is now apparent that the nature of the pentadentate ligand in the solvato Mn(II) starting material (such as $[Mn(SBPy_3)(MeOH)]^{2+}$) modulates its reactivity with NO(g). In case of **3** and **4**, the solvato species react with NO(g) within minutes while in the present case, the Mn(II) Schiff base complexes require 24 to 72 h to react with NO.

Structures of the Complexes. $[Mn(SBPy_3)(NO)](ClO_4)_2$ (1). In **1**, the Mn(II) center exists in a distorted octahedral environment with the imine N trans to NO, and the remaining N donors are coordinated in the equatorial plane (Figure 1). This coordination geometry of the $SBPy_3$ ligand is also observed in the starting complex **5** and corresponding iron complex $[Fe(SBPy_3)(CN)]BF_4$.[35] The Mn−N bond distances of **1** are uniformly shorter

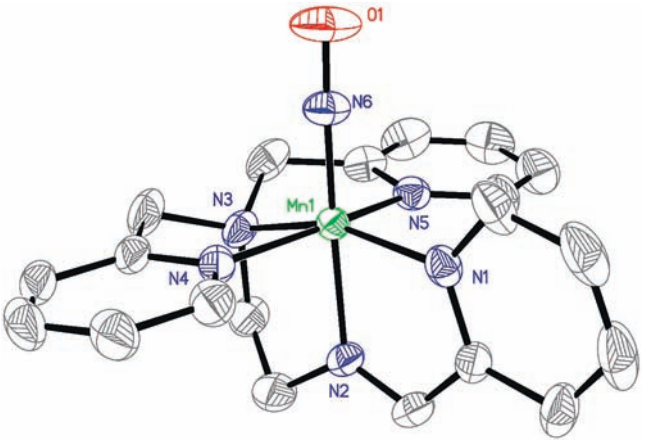


Figure 1. Thermal ellipsoid (probability level 30%) plot of $[Mn(SBPy_3)(NO)]^{2+}$ (cation of **1**) with the atom-labeling scheme. All H atoms have been omitted for the sake of clarity.

than those of **5** because of the presence of low-spin Mn(II) center in the former (vide infra). For example the $Mn-N_{imine}$ bond is 2.257(5) Å long in the chloride complex **5** while the same distance in the NO complex **1** is 1.985(4) Å. Close scrutiny of the metric parameters of **1** with those of **3** reveals that the $Mn-N_{imine}$ distance (1.985(4) Å) is noticeably longer than the $Mn-N_{amido}$ distance (1.9551(14) Å) although both N donors are trans to NO. This is most possibly due to the anionic nature of the carboxamido-N donor, a stronger σ-donor compared to the imine-N. That the carboxamido-N in **3** exerts a strong trans effect is illustrated by the longer Mn−NO and N−O bonds (1.6601(14) and 1.1918(18) Å, respectively) compared to **1** (1.649(4) and 1.167(6) Å, respectively). The slight elongation of the N−O bond is consistent with the shift in ν_{NO} observed (Figure 3a) for these two nitrosyls (1745 cm^{-1} for **3** compared to 1773 cm^{-1} for **1**). The Mn−NO unit in **1** is nearly linear at 177.2(4)°, while that of **3** is in a more bent configuration (171.91(13)°).

$[Mn(SBPy_2Q)(NO)](ClO_4)_2$ (2). The Mn center of **2** is in a distorted octahedral environment with the $SBPy_2Q$ ligand coordinated in the same fashion as observed in **1**. However, the outermost ring of the quinoline moiety is positioned above the equatorial plane (Figure 2). Comparison of the metric parameters of **2** and **4** reveals that once again the $Mn-N_{imine}$ distance (2.092(3) Å) is longer than the $Mn-N_{amido}$ distance (1.956(3) Å). In addition, the Mn−NO and N−O bonds of **2** (1.651(4) and 1.179(4) Å, respectively) are shorter than those of **4** (1.678(3) and 1.237(18) Å, respectively) because of the trans effect of the carboxamido-N donor in the latter nitrosyl. As a consequence, the ν_{NO} value of **2** (1759 cm^{-1}) is noticeably higher than that of **4** (1725 cm^{-1}, Figure 3b). The Mn−NO unit in **2** is more linear (Mn−N−O angle = 175.3(3)°) compared to that in **4** is (171.5(8)°).

To date, only one other $\{Mn\text{-}NO\}^6$ nitrosyl has been reported that is derived from a Schiff base ligand. The pentadentate ligand SB_2Py_2NH (2,12-Di(2′-pyridyl)-3,7,11-triazatrideca-2,11-diene) coordinates to the Mn(II) center of $[Mn(SB_2Py_2NH)(NO)](ClO_4)_2$ through two imine nitrogens, two pyridyl nitrogens, and a secondary amine nitrogen.[38]

(38) Cooper, D. J.; Ravenscroft, M. D.; Stotter, D. A.; Trotter, J. J. *Chem. Res.* (*S*) **1979**, 287.

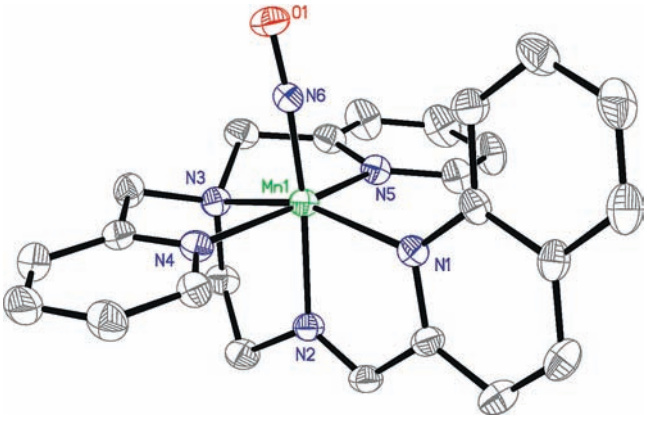


Figure 2. Thermal ellipsoid (probability level 30%) plot of $[Mn(SBPy_2Q)(NO)]^{2+}$ (cation of **2**) with the atom-labeling scheme. All H atoms have been omitted for the sake of clarity.

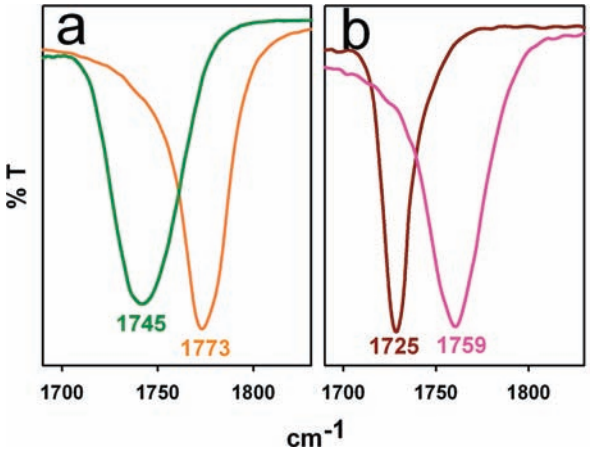
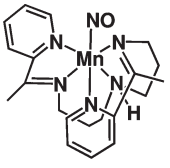


Figure 3. NO stretching frequency (ν_{NO}) of (a) **1** (orange) and **3** (green) and (b) **2** (pink) and **4** (dark red) in KBr pellet.

In this nitrosyl, the two imine nitrogens are trans to each other and the NO is trans to a pyridyl nitrogen (as shown below). The $Mn-N_{imine}$ distance of **1** (1.985(4) Å) falls between the two $Mn-N_{imine}$ distances of $[Mn(SB_2Py_2NH)(NO)](ClO_4)_2$ (1.93(3) and 2.07(3) Å). The NO ligand is bound tighter to the Mn center in $[Mn(SB_2Py_2NH)(NO)](ClO_4)_2$, as evidenced by the Mn−NO bond distance of 1.58(3) Å compared to 1.649(4) Å in **1** and 1.651(4) Å in **2**.



$[Mn(SB_2Py_2NH)(NO)]^{2+}$

The N−O bond distance in $[Mn(SB_2Py_2NH)(NO)](ClO_4)_2$ is longer (1.23(6) Å) than the same distance in **1** (1.167(6) Å) and **2** (1.179(4) Å).

Spectroscopic Properties. Coordination of the imine nitrogen to the Mn(II) center in both **1** and **2** is evidenced by a shift of ν_{CN} to lower energy (~1610 cm^{-1}) compared to 1645 cm^{-1} for the free ligands $SBPy_3$ and $SBPy_2Q$. Complexes **1** and **2** exhibit strong ν_{NO} stretches at 1773 cm^{-1} and 1759 cm^{-1}, respectively (Figure 3). As

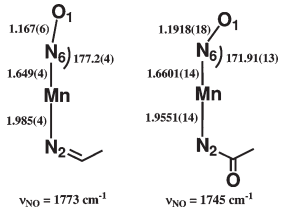


Figure 4. Comparison of bond distances (Å) and bond angles (deg) of **1** and **3**.

discussed in our previous accounts, these ν_{NO} values are typical of $\{Mn\text{-}NO\}^6$ nitrosyls with strongly coupled {low-spin Mn(II)-NO•}formulation.[26,29] $[Mn(SB_2Py_2NH)(NO)](ClO_4)_2$, the only other reported Schiff base species, also displays its ν_{NO} at 1772 cm^{-1}. In contrast, [Mn(TC-5,5)(NO)], a nitrosyl with {high-spin Mn(III)-NO^-}formulation, exhibits its ν_{NO} at 1662 cm^{-1}.[39]

A close scrutiny of the structures of the Schiff base ligands ($SBPy_3$ and $SBPy_2Q$) and the carboxamide ligands ($Papy_3H$ and $PaPy_2QH$) provides an explanation for the higher ν_{NO} values in case of the former. The ν_{NO} stretching frequency values of Figure 3a suggest that the bound NO in **1** (1773 cm^{-1}) backdonates more of its π^* electron density into the Mn−NO bond compared to **3** (1745 cm^{-1}). The same trend is observed in the two $\{Mn\text{-}NO\}^6$ nitrosyls **2** and **4**; more π-backdonation ($d\pi$-$p\pi^*$) is evident in **2** (1759 cm^{-1}) compared to **4** (1725 cm^{-1}) (Figure 3b). Since the deprotonated carboxamido-N (trans to the bound NO ligand in **3** and **4**) is a strong σ-donor, it transfers more electron density to the metal center which in turn, accepts less π^* electron density from the bound NO compared to the corresponding Schiff base species **1** and **2**. As discussed above, the structural parameters of **1**−**4** also supports this conclusion. For example, the $Mn-N_{imine}$ distance (1.985(4) Å) of **1** is noticeably longer than the $Mn-N_{amido}$ distance (1.9551(14) Å) of **3** (Figure 4) although both N donors are trans to NO. Very similar behavior has been observed in $[Ru(PaPy_3)(NO)](BF_4)_2$ and $[Ru(SBPy_3)(NO)](BF_4)_3$.[21,22c]

Strong coupling between the low-spin $S = 5/2$ Mn(II) centers with the unpaired electron of NO in **1** and **2** is further supported by the observed diamagnetism of these two $\{Mn\text{-}NO\}^6$ nitrosyl both in solid state and in solution. The $S = 0$ ground state of **1** and **2** is confirmed by their ^1H NMR spectra in CD_3CN (Figure 5, solutions prepared and run in the dark). This type of spin-coupling has been previously observed with **3** and **4** and discussed in detail.[28,29]

Electronic Absorption Spectra. Our previously reported $\{Mn\text{-}NO\}^6$ nitrosyls **3** and **4** display two distinct absorption bands (λ_{max} at 440 and 635 nm for **3**, λ_{max} at 500 and 670 nm for **4**) in the visible region. In case of the present two nitrosyls **1** and **2**, the absorption bands shift further to the tail-end of the visible region and move into the NIR region. As a result, all four $\{Mn\text{-}NO\}^6$ nitrosyls dissolve in MeCN to afford distinctly different colored solutions (Figure 6). The orange solution of **1** in MeCN exhibits its absorption bands with λ_{max} located at 500 and 720 nm while the fuchsia solution of **2** in MeCN exhibits its

(39) Franz, K. J.; Lippard, S. J. *J. Am. Chem. Soc.* **1998**, *120*, 9034.

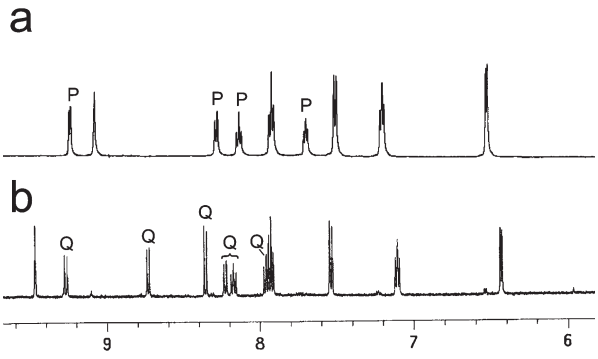


Figure 5. ^{1}H NMR Spectra (500 MHz) of (a) $[Mn(SBPy_3)(NO)](ClO_4)_2$ (**1**) and (b) $[Mn(SBPy_2Q)(NO)](ClO_4)_2$ (**2**) in CD_3CN (298 K) from 6 to 10 ppm (P and Q refer to resonances of the pyridine and quinoline portion of the imine arm of the ligands $SBPy_3$ and $SBPy_2Q$, respectively).

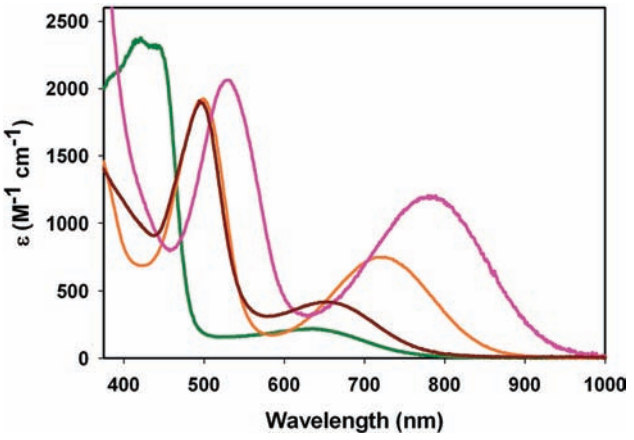


Figure 6. Comparison of the electronic absorption spectra of $[Mn(SBPy_3)(NO)](ClO_4)_2$ (**1**, orange trace), $[Mn(SBPy_2Q)(NO)](ClO_4)_2$ (**2**, pink trace), $[Mn(PaPy_3)(NO)]ClO_4$ (**3**, green trace), and $[Mn(PaPy_2Q)(NO)]ClO_4$ (**4**, dark red trace) in MeCN.

absorption bands with λ_{max} located at 550 and 785 nm. It is important to note here that both **1** and **2** exhibit a significant red shift in the low-energy band compared to **3** and **4** upon replacement of the carboxamide group with the imine group in the ligand framework. Indeed, **1** and **2** are the first examples of metal nitrosyls that exhibit strong absorption bands at such a low energy region. In addition, the extinction coefficient values of the lowest-energy band of these two Schiff base complexes are almost three times the values of the corresponding complexes derived from carboxamide ligands (Figure 6).

NO Photolability of 1 and 2. Both **1** and **2** are sensitive to light, particularly when present in solution. Complex **1** is stable in H_2O and MeCN solution for weeks at room temperature when kept in the dark. In comparison, while the solution of **2** in MeCN is quite stable (for days in the dark), aqueous solution of this nitrosyl decomposes within 2 h even in the dark (as monitored by its absorption spectrum). When solutions of **1** and **2** in MeCN are exposed to low-intensity NIR light, rapid release of NO is noted (detected by an *ami*NO-2000 electrode, Figures 7). The NO loss is clearly evident by the bleaching of the highly colored solutions in both cases. The NO chronoamperograms (one shown in Figure 7) demonstrate that both nitrosyls are very sensitive to 780 nm (5 mW) light and exhibit a linear on−off response to

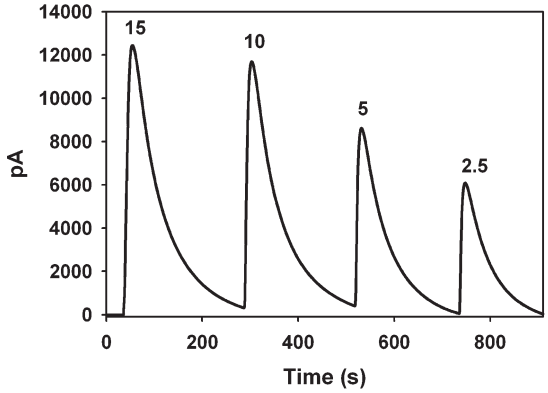


Figure 7. Chronoamperogram recorded with *amino*-2000 electrode during photodissociation of NO from **2** in MeCN under illumination with 780 nm light (5.0 mW). The numbers above the peaks indicate the number of seconds of illumination.

Table 3. Quantum Yields (Φ) for Photoreactions of Complexes **1**−**4** in MeCN

complex	λ_{irr} (nm)	Φ (mol/einst)
1	500	0.411 ± 0.010
1	550	0.580 ± 0.010
2	500	0.393 ± 0.010
2	550	0.434 ± 0.010
3	500	0.326 ± 0.010
3	550	0.309 ± 0.010
4	500	0.623 ± 0.010
4	550	0.579 ± 0.010

illumination. This confirms that the release of NO from **1** and **2** can be triggered by NIR light. As discussed before, the light-induced NO loss from **1**−**4** follows eq 1 under such conditions.[26,29]

$$[Mn(SBPy_2Q)(NO)]^{2+} \xrightarrow[h\nu]{MeCN} [Mn(SBPy_2Q)(MeCN)]^{2+} + NO \quad (1)$$

Quantum Yield Measurements. Quantum yield values (Φ) for the generation of NO from **1**, **2**, **3**, and **4** are listed in Table 3. These values were determined from changes in electronic spectra upon exposure to light of two different wavelengths (500 and 550 nm) in MeCN. Since complex **2** exhibits slow decomposition in aqueous solution even under dark conditions, the Φ values were not measured in water. Previously reported Φ values of **3** and **4** clearly showed that the incorporation of a quinolyl-carboxamide moiety in place of the pyridyl-carboxamide unit is effective not only in moving the photosensitivity toward light of longer wavelengths but also in improving Φ values for the corresponding $\{Mn\text{-}NO\}^6$ nitrosyl.[29] In case of the Schiff base nitrosyls **1** and **2**, incorporation of the quinolyl-imine moiety also shifts the photosensitivity of **2** toward light of longer wavelengths. However, **1** exhibits higher Φ values at both 500 and 550 nm compared to that of **2** (Table 3). Inspection of the Φ values of Table 3 reveals that the present two $\{Mn\text{-}NO\}^6$ nitrosyls **1** and **2** have high Φ values at both 500 nm (0.411, 0.393 respectively) and 550 nm (0.580, 0.434 respectively). At 550 nm, **1** and **4** exhibit very similar Φ values while at 500 nm, **4** is the most efficient NO donor.

Kinetic Measurements. Although **1** and **2** exhibit strong absorption bands in the 650−950 nm region (Figure 6),

Table 4. Apparent Rate of NO Photorelease (k_{NO})[a] from $[Mn(SBPy_3)(NO)](ClO_4)_2$ (**1**), $[Mn(SBPy_2Q)(NO)](ClO_4)_2$ (**2**), $[Mn(PaPy_3)(NO)]ClO_4$ (**3**), and $[Mn(PaPy_2Q)(NO)]ClO_4$ (**4**) in MeCN[b]

complex	power (mW)	λ_{irr} (nm)	$k_{NO} \times 10^{-5}$ (s^{-1})
1	1.7	450	159 ± 0.1
2			126 ± 0.1
3			83.3 ± 0.1
4			169 ± 0.1
1	1.7	500	161 ± 0.1
2			154 ± 0.1
3			12.6 ± 0.1
4			244 ± 0.1
1	1.0	550	56.9 ± 0.1
2			160 ± 0.1
3			18.1 ± 0.1
4			56.8 ± 0.1
1	1.0	600	21.1 ± 0.1
2			55.3 ± 0.1
3			19.1 ± 0.1
4			96.7 ± 0.1
1	1.0	700	9.71 ± 0.04
2			37.4 ± 0.1
3			N/A
4			72.8 ± 0.1
1	1.0	800	4.40 ± 0.05
2			22.8 ± 0.1
3			N/A
4			10.9 ± 0.1
1	3.0	900	N/A
2			23.4 ± 0.1
3			N/A
4			N/A
1	2.3	950	N/A
2			12.2 ± 0.1
3			N/A
4			N/A

[a] The rate constants only serve as a relative estimation of their capacities of NO release at various wavelengths of light under the same conditions and are not intended to be quantitative. N/A: measurements were not reliable because of very low absorbance in this region. [b] Concentration of **1**−**4** = 1 mM.

the lack of reliable chemical actinometer(s) in the NIR region restricted our Φ value measurements in this range. To establish and compare the NIR sensitivity of all four $\{Mn\text{-}NO\}^6$ nitrosyls, we have therefore measured the apparent rates of NO loss (k_{NO}) under low power (1−3 mW) lights of selected frequencies in the 450−950 nm range. The light-induced NO loss from the four nitrosyls has been monitored by recording the electronic spectra of samples after irradiation for specific periods of time. Such light-induced NO loss from **1**, **2**, **3**, and **4** all follows a pseudo-first order behavior in MeCN (Table 4).

Certain conclusions regarding the capacities of NO photorelease of these $\{Mn\text{-}NO\}^6$ nitrosyls can be drawn from the data shown in Table 4. For example, it is clear that in the range 900−950 nm, **2** retains moderate capacity of NO photorelease while the other three nitrosyls are hardly photosensitive. Interestingly, **4** releases small amounts of NO upon exposure to 800 nm light even though it has very little absorbance at that wavelength. Also, the k_{NO} values of **1** and **2** in the 550−800 nm region confirms that the introduction of the quinolyl-imine moiety in **2** indeed improves its capacity of NO photorelease. This improvement presumably arises from the higher extinction coefficient values of **2** compared to **1** in this range (Figure 6).

Overall, the data shown in Table 4 demonstrate that all the four $\{Mn\text{-}NO\}^6$ nitrosyls are good NO donors under illumination with visible light. However, when the ligand frame is changed from the carboxamide-type ($PaPy_3^-$ and $PaPy_2Q^-$) to Schiff bases ($SBPy_3$ and $SBPy_2Q$), the nitrosyls become more sensitive to NIR light (800−950 nm) and **2** *is the most sensitive nitrosyl to NIR light reported so far*. We have previously shown that **3** can be used to deliver NO to biological targets such as proteins[27,29] and tissues[34] under the control of visible light. It is now anticipated that manganese nitrosyls like **1** and **2** can be used for such purpose via triggering with NIR light. At present, such studies are in progress in this laboratory.

Summary and Conclusions

The following are the summary and conclusions of this work.

(a) Two $\{Mn\text{-}NO\}^6$ nitrosyls, namely, $[Mn(SBPy_3)(NO)](ClO_4)_2$ (**1**) and $[Mn(SBPy_2Q)(NO)](ClO_4)_2$ (**2**), have been synthesized from the Schiff base ligands $SBPy_3$ and $SBPy_2Q$. Although the ligand $SBPy_3$ has been reported previously,[26] $SBPy_2Q$ is reported here for the first time.

(b) The structures of **1** and **2** have been determined by X-ray crystallography. In both cases, the Mn−N−O angle is close to 180°. The $Mn-N_{imine}$ bonds of **1** and **2** (1.985(4) and 2.092(3) Å, respectively) are longer than $Mn-N_{amido}$ bonds present in the $\{Mn\text{-}NO\}^6$ nitrosyls derived from analogous carboxamide ligands, namely, $[Mn(PaPy_3)(NO)]ClO_4$ (**3**) and $[Mn(PaPy_2Q)(NO)]ClO_4$ (**4**).

(c) Much like **3** and **4**, the present nitrosyls **1** and **2** are diamagnetic and exhibit strong ν_{NO} at 1773 and 1759 cm^{-1} respectively. The $S = 0$ ground state of these nitrosyls suggests a strongly coupled {low-spin Mn(II)-NO•}formulation.[26]

(d) Both **1** and **2** are very sensitive to low-power (1−5 mW) visible and NIR light. Their capacity of NO photorelease under NIR light in the 800−950 nm range is particularly noteworthy. The nitrosyl **2** releases NO quite rapidly when exposed to 950 nm light. The previously reported nitrosyls **3** and **4** exhibit little or no NO photorelease in this range.

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Supporting Information Available: X-ray crystallographic data (in CIF format) for $[Mn(SBPy_3)(NO)](ClO_4)_2$ (**1**) and $[Mn(SBPy_2Q)(NO)](ClO_4)_2 \cdot CH_3CN$ (**2**·CH_3CN). This material is available free of charge via the Internet at http://pubs.acs.org.