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Supporting Information

Visible-light driven photocatalytic CO_2 reduction promoted by organic photosensitizers and a Mn(I) catalyst

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Materials

All the reagents were purchased from commercial sources (Sigma-Aldrich, Alfa Aesar, TCI) and used without further purification.

Photophysical measurements

UV-Vis absorption spectra were recorded with a PerkinElmer λ40 spectrophotometer or with a JASCO V-565 spectrophotometer using quartz cells with optical path length of 1.0 cm. Emission spectra were measured using a HORIBA Fluorolog-3-21 spectrofluorometer. Emission lifetimes were determined with a HORIBA FluoroCube time-correlated single-photon counting system or with an Edinburgh FS5 spectrofluorometer equipped with a Hamamatsu Photomultiplier R928P phototube and with a TCC900 card for data acquisition in TCSPC. Emission quantum yields were determined using a HAMAMATSU UV-NIR Absolute PL Quantum Yield Spectrometer C13534. The estimated experimental errors are: 2 nm on the band maximum, 5% on the molar absorption coefficient and luminescence lifetime, 10% on the emission quantum yield in solution. Degassed solutions for mechanistic studied were obtained by five freeze-pump-thaw cycles.

Electrochemical experiments

The redox potentials of the photosensitizers were measured in an Ar-saturated DMA solution containing the analyte (0.5 mM) and Et_4NBF_4 (0.1 M) as a supporting electrolyte by cyclic voltammetric techniques using an ALS CHI-620Ex electrochemical analyzer with a glassy carbon disk working electrode (3 mm diameter), an $Ag/AgNO_3$ (0.01 M) reference electrode, and a Pt counter electrode. The supporting electrolyte was dried under vacuum at 100 °C overnight prior to use. The scan rate was 200 $mV \cdot s^{-1}$.

Photocatalytic reactions

Photocatalytic reactions were performed in a DMA solution containing the organic photosensitizer (250 μM or 50 μM), **Mn** (50 μM), BIH (0.1 M), and TEOA (1.5 M). The solution was purged with CO_2 for 20 min and then irradiated. In order to determine the turnover number, 2 mL solutions in an 11-mL test tube (internal diameter = 8 mm) were irradiated using a merry-go-round type irradiation apparatus with LED light, Iris-MG (CELL System co.). In order to determine quantum yields, 4 mL solution in a quartz cubic cell (11 mL, light-pass length: 1 cm) was irradiated using a Shimadzu photoreaction quantum yield evaluation system, QYM-01 that measured absorbance of the reaction solution at λ_{ex} = 480 nm 10 times during irradiation, and these data were used to calculate absorbed photon numbers to the reaction solution. The temperature of the solution was controlled during irradiation at 25 ± 0.1°C using an IWAKI CTS-134A constant-temperature system. The gaseous products of photocatalysis, i.e., CO and H_2, were analyzed by GC-TCD (GL science GC323). Formic acid was analyzed using a capillary electrophoresis system (Agilent technology 7100L).

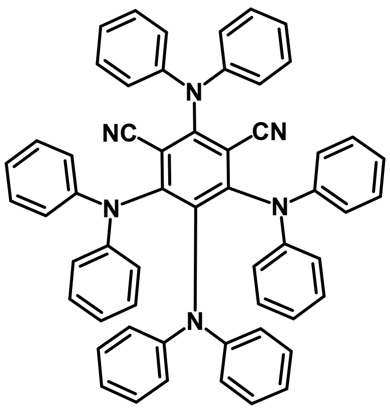
Labeling experiments using $^{13}CO_2$

A DMA solution of **4DPAIPN** (250 μM), **Mn** (250 μM), BIH (0.1 M), and TEOA (1.5 M) was deaerated three times via a freeze–pump–thaw cycles before adding $^{13}CO_2$ (662 mmHg). The solution was irradiated at λ_{ex} = 470 nm using LED for 20 h. The gas phase was analyzed by GC-MS (Shimadzu GCMS-QP2010 equipped with a MS-5A column (i.d. 0.32 mm, 30.0 m)). Formic acid was extracted with ethyl acetate prior to the GC-MS analyses as follows. A portion of the resulting solution (1 mL) was placed in a sample tube. After adding 1 mL of water, 1.0 M sulfuric acid was added to adjust pH = 3. Ethyl acetate (3 mL) was added, and the mixed solution was shaken for 1 min and stood for 1 min to extract formic acid into the ethyl acetate phase. The ethyl acetate phase was analyzed using Shimadzu GCMS-QP2010 equipped with a SH-1 column (i.d. 0.32 mm, 60.0 m).

Synthesis

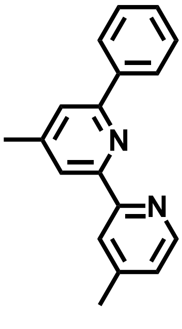
2,4,6-tri(diphenylamino)-5-fluoroisophthalonitrile (**3DPAFIPN**), 2,4,5,6-tetrakis(carbazol-9-yl)-isophthalonitrile (**4CzIPN**), 2,3,4,5,6-penta(carbazol-9-yl)-benzonitrile (**5CzBN**) and 2,4,6-tri(carbazol-9-yl)-5-chloroisophthalonitrile (**3CzClIPN**) were prepared according to published literature procedures.[1]

2,4,5,6-tetrakis(diphenylamino)-isophthalonitrile (4DPAIPN)



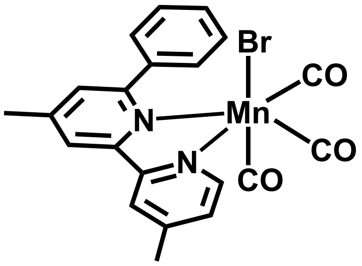
A modified literature procedure was adopted for the synthesis of **4DPAIPN**.[2] A 50 mL round-bottom flask was filled with dry DMF (10 mL) and diphenylamine (5.6 mmol, 948 mg, 6 equiv.) under inert atmosphere. NaH (60% suspension in mineral oil, 7.5 mmol, 300 mg, 8 eq.) was slowly added and the mixture was stirred at 50 °C for 5 hours. 2,4,5,6-tetrafluoroisophthalonitrile (0.9 mmol, 187 mg, 1 equiv.) was added and the reaction mixture was stirred at 90 °C for 8 hours. After that, the solution was cooled to 0°C and water (1 mL) was slowly added to quench the reaction. A yellow precipitate appeared upon addition of MeOH (10 mL) and was collected by filtration. The solid was redissolved in DCM (10 mL) and reprecipitated by the addition of MeOH (10 mL) to afford the desired clean product (Yield: 60%, 0.54 mmol, 431 mg). Spectroscopic data are in agreement with those reported in literature.[2]

6-phenyl-4,4′-dimethyl-2,2′-bipyridine (^{6}Phdmb)



A Schlenk flask containing 6-bromo-4,4′-dimethyl-2,2′-bipyridine (1.20 g, 4.56 mmol), phenylboronic acid (0.870 g, 7.14 mmol), $Pd(PPh_3)_4$ (0.305 g, 0.264 mmol) and Na_2CO_3 (2.1 g, 20 mmol) was evacuated and filled with Ar. Dry 1,4-dioxane (25 mL) and degassed H_2O (5 mL) by bubbling with Ar were added, and the mixture was heated to 90 °C for 16.5 h under an Ar atmosphere. After cooling to room temperature, the solvent was removed and dichloromethane and H_2O were added. The extracted layer of dichloromethane was dried over Na_2SO_4 and dichloromethane was evaporated. The product was purified by silica-gel column chromatography (eluent: dichloromethane ~ dichloromethane–methanol (2%)) and recrystallized from ethanol. Yield: 0.995 g (3.82 mmol, 84%). ^{1}H NMR (400 MHz, chloroform-*d*) δ/ppm: 8.54 (d, J = 5.0 Hz, 1H), 8.44 (d, J = 0.9 Hz, 1H), 8.20 (s, 1H), 8.13 (d, J = 7.6 Hz, 2H), 7.59 (s, 1H), 7.51 (dd, J = 8.0, 7.2 Hz, 2H), 7.43 (dd, J = 7.2, 6.8Hz, 1H), 7.14 (d, J = 5.0 Hz, 1H), 2.50 (s, 3H), 2.48 (s, 3H).

***fac*-Mn(^{6}Phdmb)(CO)$_3$Br (Mn)**



$Mn(CO)_5Br$ (60.3 mg, 0.219 mmol) and 6-phenyl-4,4′-dimethyl-2,2′-bipyridine (55.8 mg, 0.214 mmol) were suspended in Ar-saturated diethylether and stirred at 40 °C for 16 h under an argon atmosphere in the dark. After cooling to room temperature, the precipitated solid was collected and washed with diethylether. Yield: 93.6 mg (0.195 mmol, 91%). ^{1}H-NMR (400 MHz, acetonitrile-d_3) δ/ppm: 9.02 (d, J = 5.8 Hz, 1H, H^6-Py), 8.24 (s, 1H, H^3-Py), 8.21 (s, 1H, H^3-Py*), 7.63-7.56 (m, 5H, Ph), 7.45 (s, 1H, H^5-Py*), 7.42 (d, J = 5.8 Hz, 1H, H^5-Py), 2.56 (s, 3H, Me-Py*), 2.55 (s, 3H, Me-Py); Py* = Ph-Py. ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm:165.2, 157.0, 156.0, 152.7, 150.1, 149.9, 142.2, 129.9, 129.3, 128.5, 126.7, 123.7, 121.8, 21.5, 21.3. FT-IR (in dichloromethane) ν_{CO} / cm^{-1}: 2025, 1939, 1912. Anal. Calcd. for $C_{21}H_{16}BrMnN_2O_3\cdot 0.5(H_2O)$: C, 51.66; H, 3.51; N, 5.74. Found: C, 51.83; H, 3.39; N, 5.57.

Experiments

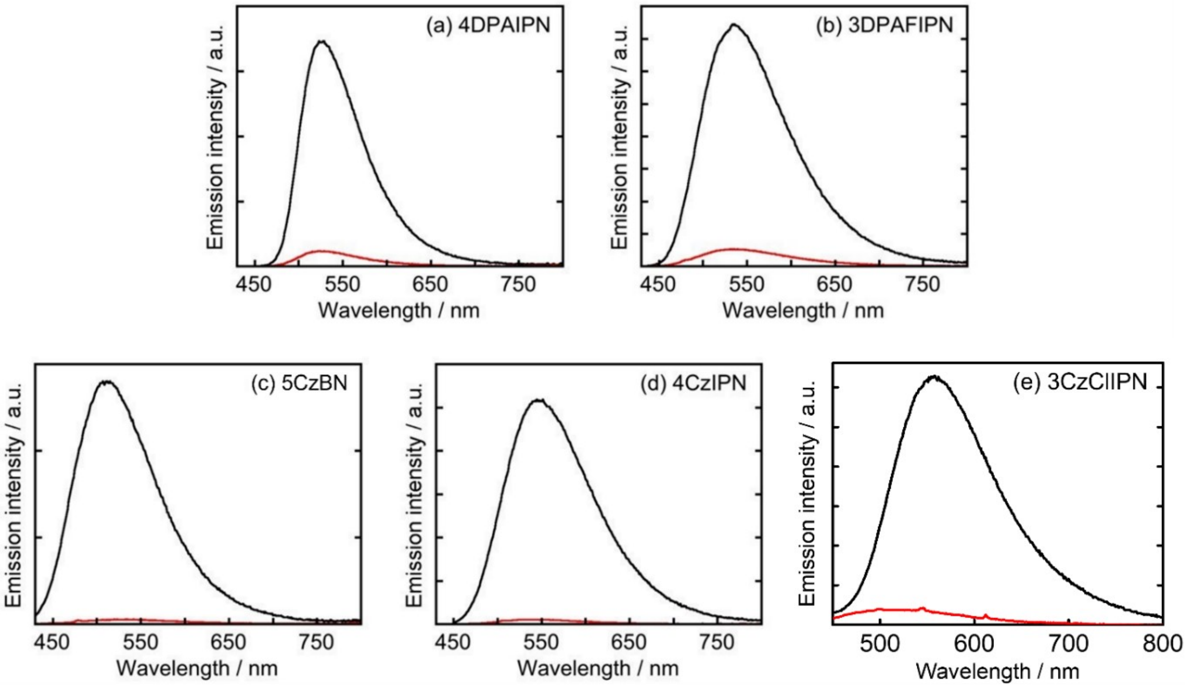


Figure S1 Emission spectra in Ar-saturated DMA (black line) and Ar-saturated DMA containing BIH (0.1 M) and TEOA (1.5 M). Excitation wavelengths were λ_{ex} = 440 nm for (a), (d), (e) and λ_{ex} = 420 nm for (b), (c).

Upon addition of TEOA (1.5 M) to a 3CzClIPN solution the maximum of the emission intensity shifted from 554 nm to 517 nm, which is likely due to the degradation of 3CzClIPN. This further supports the fact that it is not a suitable photosensitizer for CO_2 reduction under the studied reaction conditions.

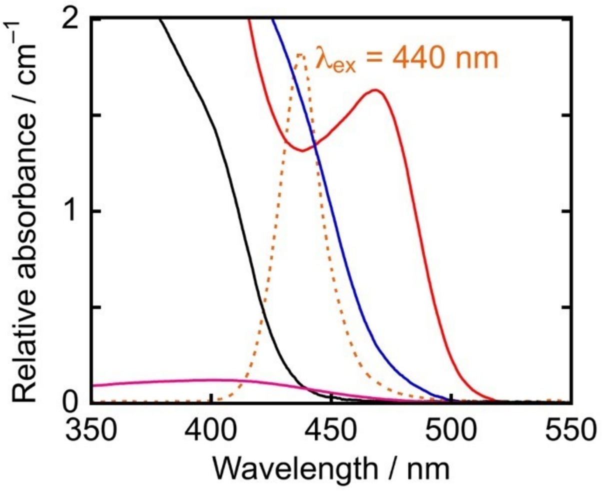


Figure S2 Relative absorption spectra of **4DPAIPN** (250 µM, red line), **3DPAFIPN** (250 µM, blue line), **5CzBN** (250 µM, black line), and **Mn** (50 µM, purple line) calculated from their molar absorption coefficients in DMA. Orange dashed line indicates the wavelength distribution of irradiated light at λ_{ex} = 440 nm in the photocatalytic reaction condition.

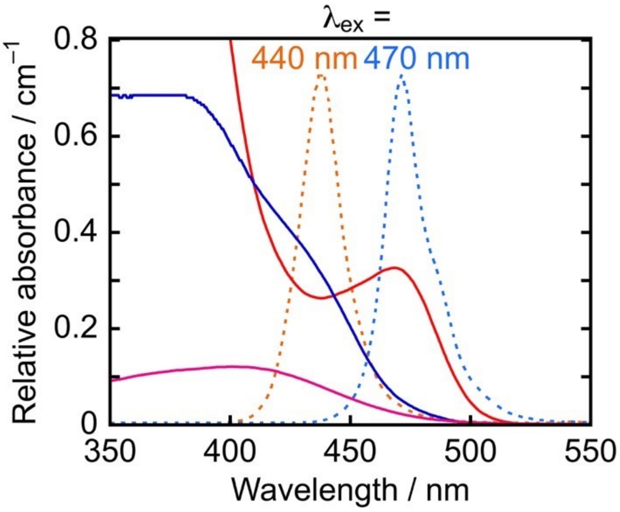


Figure S3 Relative absorption spectra of **4DPAIPN** (50 µM, red line), **3DPAFIPN** (50 µM, blue line), and **Mn** (50 µM, purple line) calculated from their molar absorption coefficients in DMA. Orange and sky blue dashed line indicates the wavelength distribution of irradiated light at λ_{ex} = 440 nm and 470 nm in the photocatalytic reaction condition.

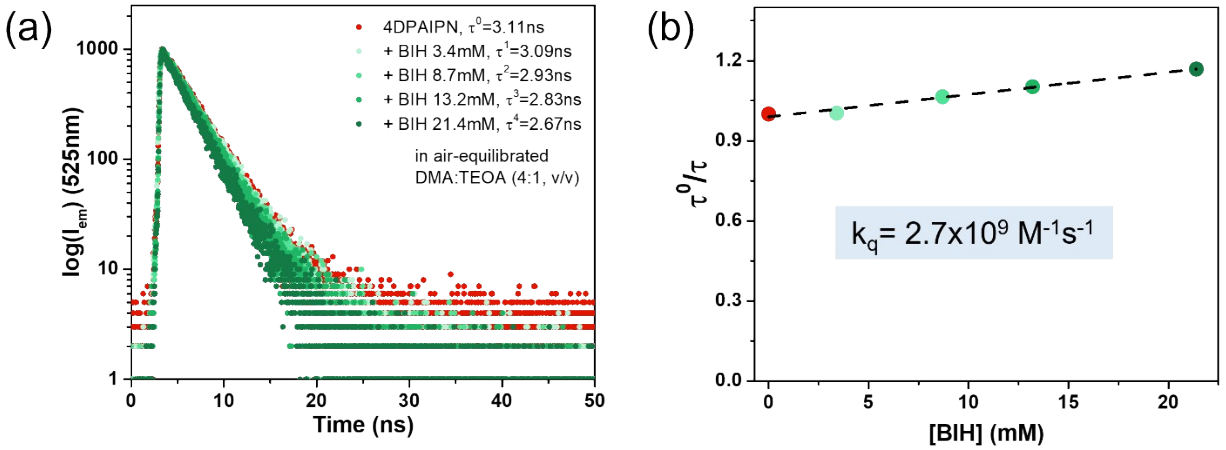


Figure S4 (a) Emission intensity decays (λ_{ex}: 405 nm; λ_{em}: 525 nm) of **4DPAIPN** upon addition of increasing amounts of BIH (up to 21 mM) in air-equilibrated DMA:TEOA (4:1, v/v). (b) Corresponding Stern-Volmer plot.

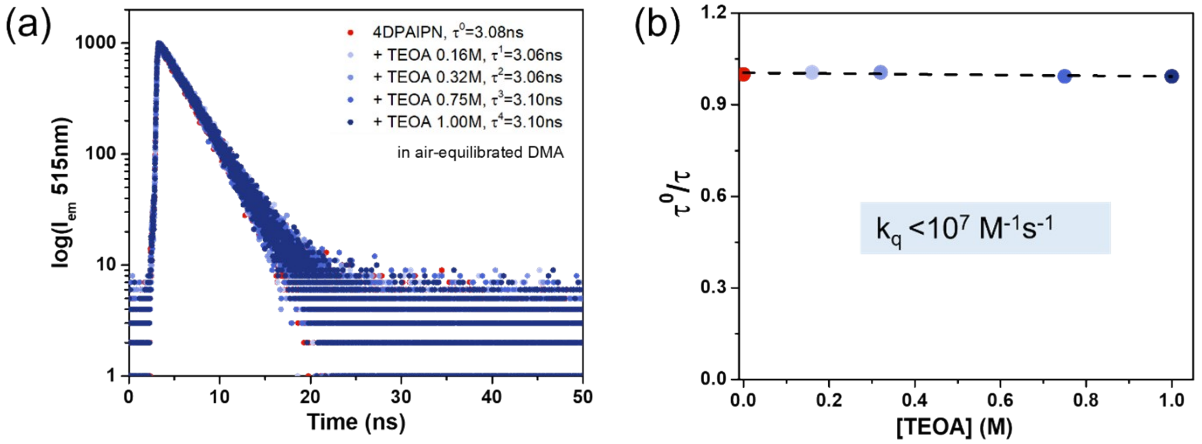


Figure S5 (a) Emission intensity decays (λ_{ex}: 405 nm; λ_{em}: 515 nm) of **4DPAIPN** upon addition of increasing amounts of TEOA (up to 1 M) in air-equilibrated DMA. (b) Corresponding Stern-Volmer plot.

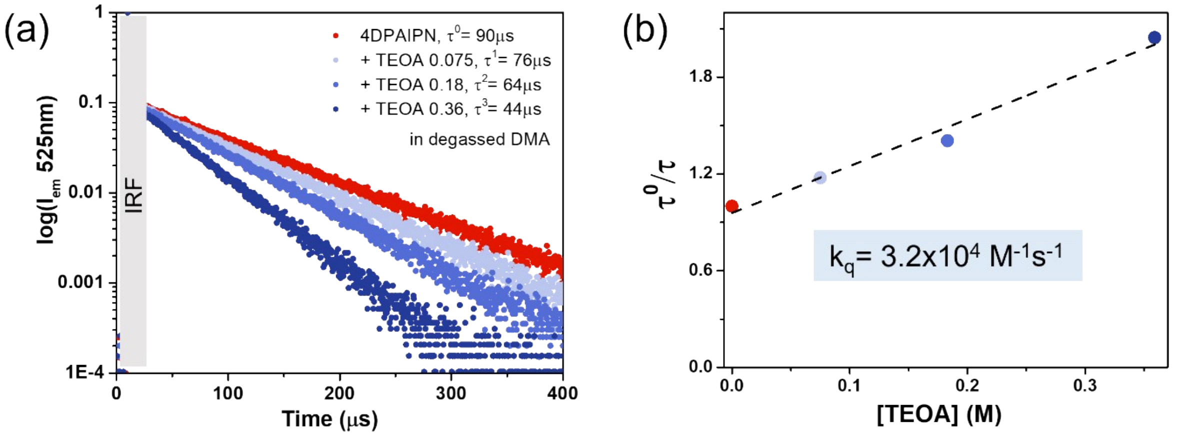


Figure S6 (a) Emission intensity decays (λ_{ex}: 470 nm; λ_{em}: 525 nm) of **4DPAIPN** upon addition of increasing amounts of TEOA (up to 0.36 M) in degassed DMA; the IRF has been grayed out. (a) Corresponding Stern-Volmer plot.

Quenching efficiency of TADF photosensitizers by species i (η^i) can be estimated according to the following formula:

$$\eta^i = \frac{k_q^i \cdot [Q]^i}{(k_{nr} + k_r) + \sum_0^n k_q^n \cdot [Q]^n}$$

Where k_q^i is the quenching constant determined by Stern-Volmer experiments of species i, $[Q]^i$ is the concentration of species i used in the reaction conditions and $(k_{nr} + k_r)$ is equal to $1/\tau$. In the latter, in order to consider the quenching efficiency of either prompt or delayed fluorescence it is important to consider τ_{FLUO} or τ_{TADF}, respectively.

Values for the reaction promoted by **4DPAIPN** in the concomitant presence of both quenchers are reported in the following table, with the value of k_q for the catalyst being estimated as the diffusional constant by using Smoluchowski's and Stokes-Einstein's equations and considering the viscosity of DMA as equal to 0.945 mPa·s.[3]

Quencher (Q)	**[Q] (M)**	**PROMPT**		**TADF**	
		k_q ($M^{-1}s^{-1}$)	**η(%)**	**k_q ($M^{-1}s^{-1}$)**	**η(%)**
TEOA	1.5	$<10^7$	0	3.2×10^4	0.3
BIH	0.1	2.7×10^9	45	1.5×10^8	97
Mn(^{6}Phbpy)(CO)$_3$Br	0.000050	7.3×10^9	0.1	7.3×10^9	2.4

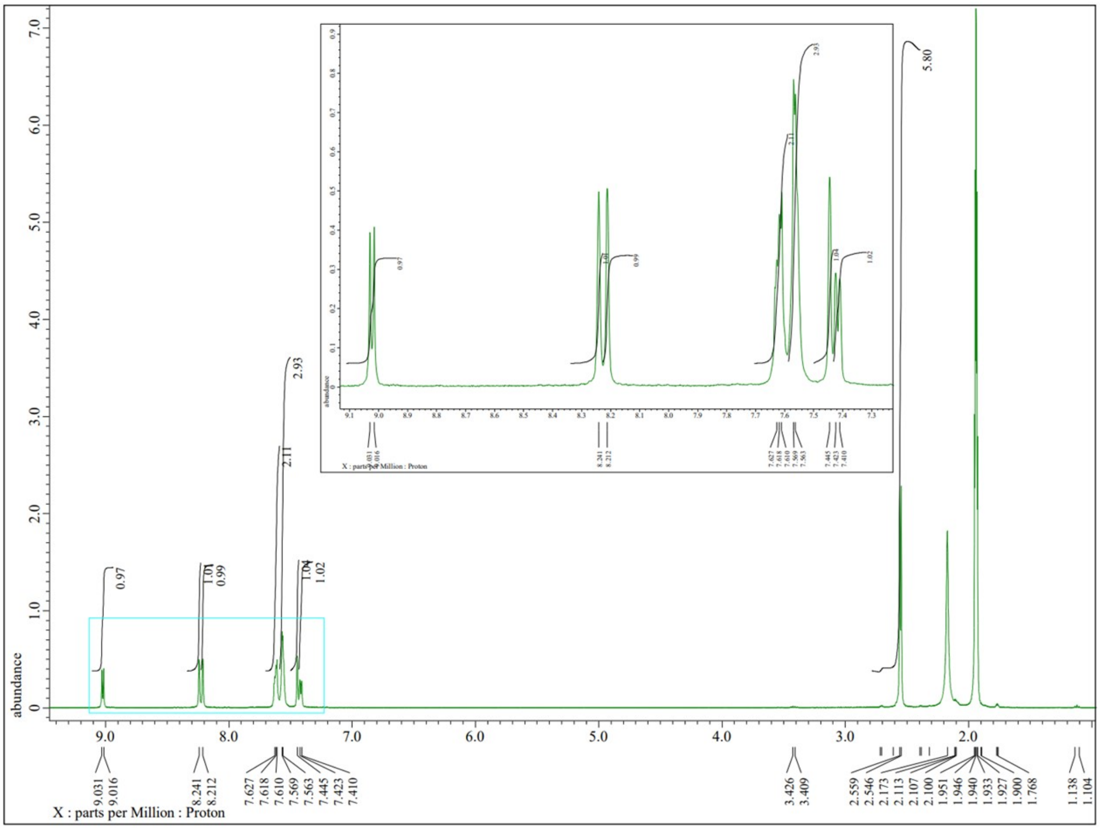


Figure S7 ^{1}H NMR spectrum of **Mn**.

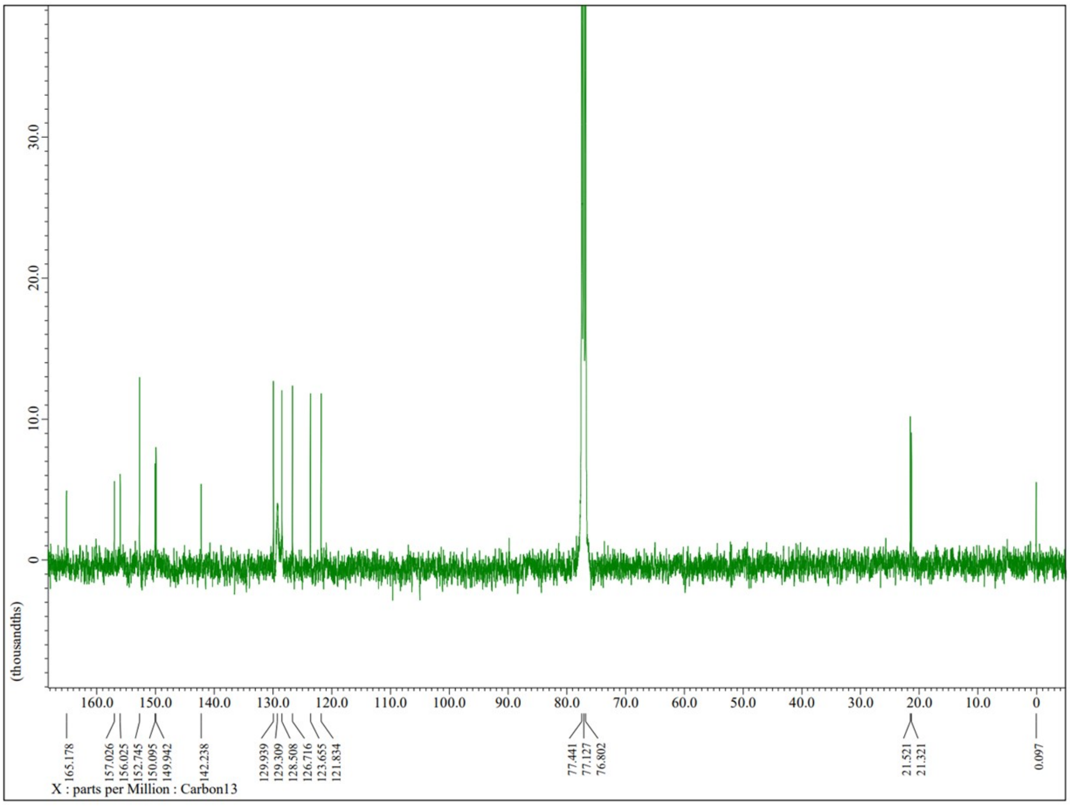


Figure S8 ^{13}C NMR spectrum of **Mn**.

References

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