Electronic Supporting Information

Green Radicals of Potassium Poly(heptazine imide) Using Light and Benzylamine

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Experimental section

Materials

Acetonitrile (≥99.8%, water content 0.005 %), acetonitrile-*d*$_3$ (≥99.8 atom % D, water content ≤0.02 %), argon 5.0 (99.999 %, water content 3 vol. ppm), carbon dioxide (99.5 %, water content 67 vol. ppm), chloroform-*d* (99.8 atom % D), (^{15}N)benzylamine (98 atom % ^{15}N), benzylamine (99%), methyl viologen dichloride hydrate (98%).

Methods

^{1}H, ^{13}C and ^{15}N NMR spectra were recorded on Agilent 400 MHz (at 400 MHz for Protons, 101 MHz for Carbon-13 and 41 MHz for Nitrogen-15). Chemical shifts are reported in ppm versus solvent residual peak: $CDCl_3$ - 7.26 ppm in ^{1}H NMR, 77.16 ppm in ^{13}C NMR; CD_3CN – 1.94 ppm in ^{1}H NMR, 1.32, 118.26 ppm in ^{13}C NMR, 44.76 ppm in ^{15}N NMR; HDO – 4.79 ppm in ^{1}H NMR.

Light source

Light intensity of the LED module was measured by PM400 Optical Power and Energy Meter equipped with the integrating sphere S142C and purchased from Thorlabs. Emission spectrum of the blue LED is shown below.

Elemental analysis was accomplished as combustion analysis using a Vario Micro device.

EPR measurements

EPR spectra at X-band (9 GHz) and room temperature were recorded on a lab-built spectrometer comprised of an ER041 MR microwave bridge with 4122 SHQE probe head, AEG electromagnet controlled by ER081S/BH15 power supply/controller (Bruker Biospin, Karlsruhe, Germany), a SR810 lock-in amplifier (Stanford Research Systems, USA), and a 53181A frequency counter (Agilent Technologies, USA). N@C60 was used as g-standard for magnetic field calibration.[1]

H_2 detection

The experiment was performed using Agilent Technologies 7890B gas chromatography system equipped with a thermal conductivity detector (TCD) allowed for analysis of the gas produced during the photocatalytic experiment. The separation of the gaseous species was performed with an Agilent select permanent gases/CO_2 capillary column set. The latter was consisting of two parallel columns that combine CP Molsive 5 Å for permanent gas analysis, and CP PoraBOnD Q for CO_2 analysis. The detector and oven temperatures used were 200 and 45 °C, respectively. Ar was used as a carrier phase with a flow rate of 14 mL min^{-1}. The injection was performed with a 250-µL gas-tight syringe from SGE Analytical Science. A calibration gas consisting of 20% CO_2, 5% CO, 5% CH_4, 2% H_2, and 1% C_2H_6 mixed in Ar, injected in known volumes, was used to obtain the calibration curve that allowed the quantification of the gas products.

Time-resolved fluorescence spectroscopy

Time-resolved fluorescence measurements were performed by using a single photon counting setup (TCSPC) with a Becker&Hickl PML-spectrometer (modified Oriel MS-125) with a laser repetition rate of 2 MHz. The detector comprises a Becker&Hickl PML-16-C-1 (modified Hamamatsu) multi-alkaline photomultiplier. The excitation wavelength was 405 nm. The excitation was carried out using a pulsed laser diode at ~30 nJ/cm^2 (LDH-P-C405, PicoQuant GmbH). The emission was recorded in the range of 460-600 nm, while blocking the secondary detection of the excitation pulses with a 450 nm cut-off-filter. Raw decay data presented as logarithm of photon counts versus time were analyzed with data analysis software of PicoQuant GmbH (Germany). The decay times were extracted by means of a reconvolution fit based on a double and triple exponential model. Considering that

$$I_{PL}(t) = \sum_{i=1}^{i=n} a_i e^{-t/\tau_i}$$

where τ_i is the lifetime and a_i is the amplitude of the ith component, the intensity-averaged fluorescence lifetime <τ> was calculated as

$$\langle\tau\rangle = \sum_{i=1}^{i=n} a_i \tau_i^2 \Big/ \sum_{i=1}^{i=n} a_i \tau_i$$

Fourier transform infrared (FT-IR) spectra were recorded on Thermo Scientific Nicolet iD5 spectrometer.

Powder X-diffraction patterns were measured on a Bruker D8 Advance diffractometer equipped with a scintillation counter detector with CuKα radiation (λ = 0.15418 nm) applying 2θ step size of 0.05° and counting time of 3s per step.

Nitrogen adsorption/desorption measurements were performed after degassing the samples at 150 °C for 20 hours using a Quantachrome Quadrasorb SI-MP porosimeter at 77.4 K. The specific surface areas were calculated by applying the Brunauer-Emmett-Teller (BET) model to adsorption isotherms for $0.05 < p/p0 < 0.3$ using the QuadraWin 5.11 software package.

Scanning electron microscopy (SEM) images were obtained on a LEO 1550-Gemini microscope.

The X-ray photoelectron spectroscopy (XPS) measurements were carried out in an ultrahigh vacuum (UHV) spectrometer equipped with a VSW Class WA hemispherical electron analyzer. A dual anode Al Kα X-ray source (1486.6 eV) was used as incident radiation. Survey and high resolution spectra were recorded in constant pass energy mode (44 and 22 eV, respectively). During the Ultraviolet Photoelectron (UP) Spectrocopy measurements (He I excitation energy $h\nu = 21.23$ eV) measurements a bias of 15.32 V was applied to the sample, in order to avoid interference of the spectrometer threshold in the UP spectra. The values of the valence band maximum (VBM) are determined by fitting a straight line into the leading edge.

Optical absorbance spectra of powders were measured on a Shimadzu UV 2600 equipped with an integrating sphere.

Emission spectra were recorded on Jasco FP-8300 instrument. The excitation wavelength was 360 nm.

Energy dispersive X-ray (EDX) analysis was performed on JEOL JSM-7500F electron microscope equipped with two Oxford Instruments EDX detectors, located at opposite sides from the sample. The angle between the sample film surface and EDX detector axis was 28°.

The TEM measurements were acquired using a double-corrected Jeol ARM200F, equipped with a cold field emission gun and a Gatan GIF Quantum. The used acceleration voltage was 200 kV and the emission was set to 10 µA in order to reduce beam damage. An objective aperture with a diameter of 60 µm was introduced into the beam to improve the contrast while still allowing for atomic resolution.

UV-vis absorption spectra of $MV^{\bullet+}$ in MeCN were recorded using T-70 spectrometer.

Steady-state fluorescence spectra of DHPIQ in MeCN (ca. 10^{-4} M) were recorded using Jasco FP-8300 fluorescence spectrometer equipped with integrating sphere. The samples were excited with 350 nm. Fluorescence internal quantum efficiency was measured using integrating sphere upon samples excitation with 360 nm.

Vials for photocatalytic tests

In this work, screw-capped tubes (total volume 5 mL) were used to perform photocatalytic experiments unless other is stated. Transmittance of the tube is shown on the Figure S1. Transmittance of the glass tube at the LED emission maximum (461 nm) is 0.97. Transmittance of the glass tube at 400 nm (the wavelength below which the light source does not emit) is 0.94.

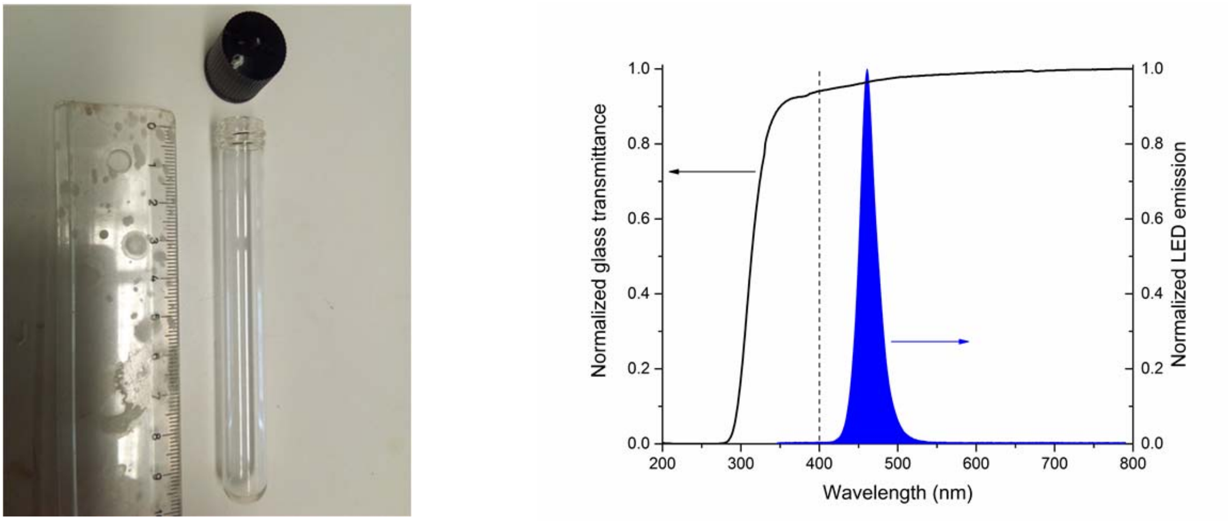


Fig. S1. Tube used in the photocatalytic experiments in this work (left). Emission spectrum of the LED module (filled) and transmission of the glass tube used for photocatalytic tests (black line) (right).

K-PHI preparation

K-PHI was synthesized according to a previously described procedure.[2] A mixture of lithium chloride (3.71 g), potassium chloride (4.54 g) and 5-aminotetrazole (1.65 g) was ground in ball mill for 5 min at the shaking rate 25 s^{-1}. Reaction mixtures were transferred into porcelain crucibles and covered with lids. Crucibles were placed in the oven and heated under constant nitrogen flow (15 $L\cdot min^{-1}$) and atmospheric pressure at a following temperature regime: heating from room temperature to 550 °C for 4 hours, annealing at 550 °C for 4 hours. After completion of the heating program, the crucibles were allowed to cool slowly to room temperature under nitrogen flow. The crude products were removed from the crucibles, washed with deionized water (100 mL) for 3 hours in order to remove salts, then filtered, extensively washed with deionized water and dried in a vacuum oven (20 mbar) at 50 °C for 15 h.

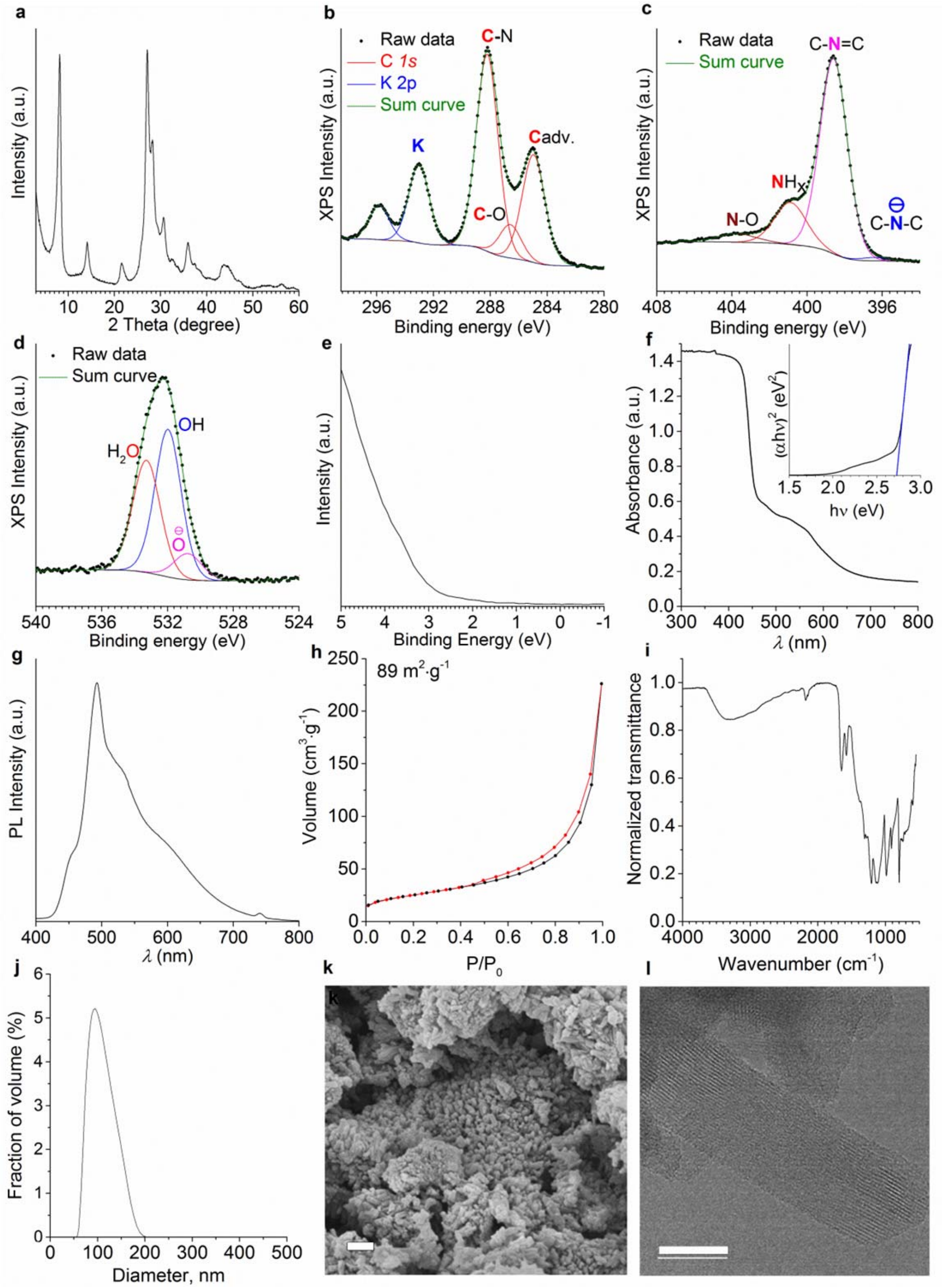


Fig. S2. K-PHI characterization data. a) PXRD pattern of K-PHI; b) XPS C 1s and K 2p spectra of K-PHI; c) XPS N 1s spectrum of K-PHI; d) XPS O 1s spectrum of K-PHI; e) UPS spectrum of K-PHI; f) UV-vis absorption spectrum of K-PHI with Tauc plot as inset assuming that K-PHI is a direct semiconductor; g) room temperature photoluminescence (PL) spectrum of K-PHI obtained upon excitation with 350 nm wavelength; h) N_2 sorption isotherm measured at 77 K. BET surface area; i) FT-IR spectrum of K-PHI; j) Dynamic light scattering (DLS) analysis of K-PHI suspension in water; k) representative SEM image of K-PHI photocatalyst. Scale bar 200 nm; l) Aberration corrected high resolution transmission electron microscopy (AC-HRTEM) image of K-PHI photocatalyst. Scale bar 20 nm.

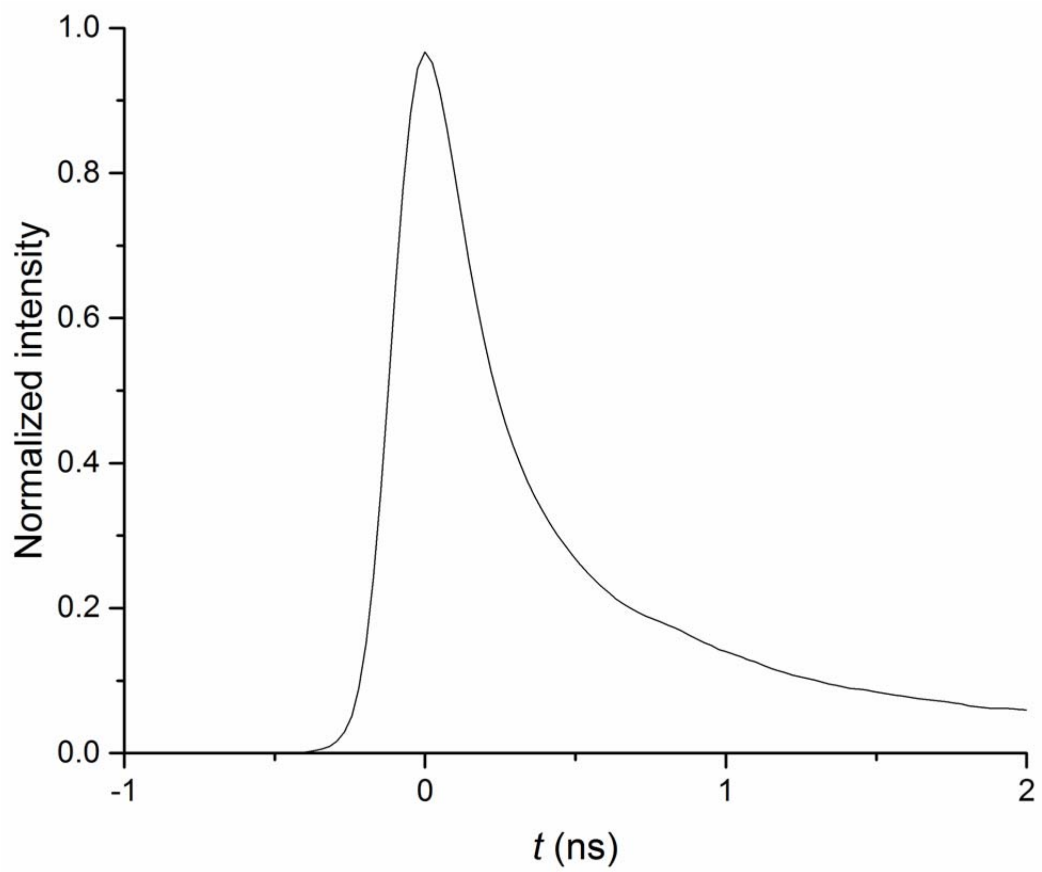


Fig. S3. Time-resolved fluorescence spectrum of K-PHI particles suspension in degassed MeCN excited with 405 nm.

Synthesis of mpg-CN

Cyanamide (3.0 g) and Ludox HS-40 (7.5 g) were mixed in a 10 mL glass vial. The mixture was stirred at room temperature for 30 min until cyanamide has completely dissolved. The resultant solution was stirred at +60°C for 16 h until water has completely evaporated. The magnetic stirrer bar was removed and white solid was transferred to the porcelain crucible and heated under N_2 flow in the oven. The temperature was increased from room temperature to 550°C within 4 h and maintained at 550°C for 4 h. The crucible was spontaneously cooled to room temperature. The solid from the crucible was briefly grinded in the mortar and transferred to the polypropylene bottle. A solution of $(NH_4)HF_2$ ($0.24\ g\cdot mL^{-1}$, 50 mL) was added and suspension was stirred at room temperature for 24 h. The solid was filtered, thoroughly washed with water, once with ethanol and dried in vacuum (55°C, 20 mbar) overnight.

A procedure of K-PHI radical anion quenching with methyl viologen

A thick-walled glass tube equipped with a Teflon valve and side arm was charged with benzylamine (0.2 mmol), K-PHI (typically 5 mg, or other mass for calibration curve on Figure 2d), MeCN (3 mL, V in the equation below) and a stir bar. The mixture was degassed using freeze-pump-thaw method (3 times, liquid nitrogen, residual pressure $7\cdot10^{-5}$ bar) and refilled with CO_2 (1 bar). The mixture was stirred at 35°C under blue LED irradiation (λ_{max} = 461 nm, $0.0517\pm3\cdot10^{-5}\ mW\cdot cm^{-2}$) for 24h. The tube with the reaction mixtures was transferred into the glove box (residual O_2 concentration <0.1 ppm, residual H_2O concentration <0.1 ppm) and 0.1 mmol of methyl viologen dichloride was added to each mixture. The tube end was covered with the PTFE-separator and firmly closed with a cap. The sealed tube was removed from the glove box and the mixture was vigorously stirred for 3 h. The color of the reaction mixture changed from greenish to deep blue. The catalyst was allowed to precipitate at the bottom of the tube. The tubes were again transferred into the glove box and solutions for UV-vis analysis were prepared: V_2 volume of the reaction mixture was taken from each tube and diluted with MeCN to the total volume V_1. These solutions in a closed screw capped QS quartz cuvette were used for UV-vis measurements. For calculations of trapped electrons average numbers of three measurements were used.

Number of electrons (μmol) trapped in K-PHI was calculated according to the equation:

$$N = \frac{A \cdot V_1}{\varepsilon \cdot L \cdot V_2} \cdot V \cdot 1000$$

A – absorbance of $MV^{\cdot+}$ solution at 605 nm; V_1 – volume of the diluted solution, which was used for the analysis, mL; V_2 – volume of the reaction mixture with $MV^{\cdot+}$ taken for analysis, mL; ε – extinction coefficient of $MV^{\cdot+}$, $M^{-1}cm^{-1}$; L – optical path of the QS quartz cuvette, cm; V – total volume of the reaction mixture, mL.

Typical procedure for preparation of imines from benzylamines

A screw-capped tube (5 mL) was charged with benzylamine (0.05 mmol), K-PHI (5 mg), MeCN (3 mL) and magnetic stir bar. The mixture was degassed using freeze-pump-thaw method (3 times, liquid nitrogen, residual pressure $7 \cdot 10^{-5}$ bar) and refilled with CO_2. The mixture was stirred at 35°C under blue LED irradiation (λ_{max} = 461 nm, $0.0517 \pm 3 \cdot 10^{-5}$ $mW \cdot cm^{-2}$) for 24h. After that time the catalyst was separated by centrifugation. The acetonitrile solution was concentrated in vacuum (50°C, 100 mbar) and analyzed by ^1H NMR in $CDCl_3$. NMR spectrum was identical to the reported earlier.[3]

^1H NMR (400 MHz, Chloroform-*d*) δ 8.40 (s, 1H), 7.78 (dd, *J* = 6.7, 2.6 Hz, 2H), 7.45 – 7.31 (m, 8H), 4.82 (s, 2H).

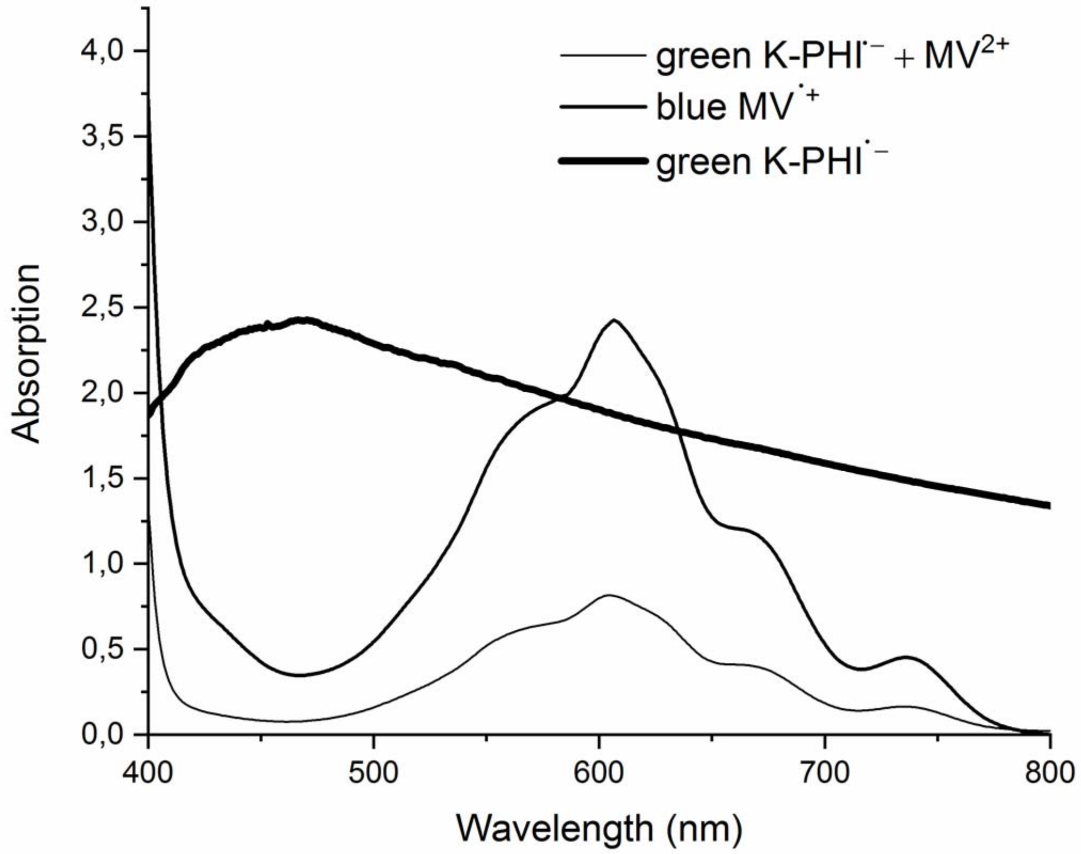


Fig. S4. Absorption spectra of green K-PHI radical anion (K-PHI$^{\cdot-}$) in MeCN; methylviologen radical cation MV$^{\cdot+}$; reaction mixture upon quenching of K-PHI$^{\cdot-}$ with methylviologen dichloride. Negligible absorbance at 800 nm of the mixtures after MV^{2+} addition suggests that K-PHI particles completely precipitated and neither K-PHI itself nor K-PHI$^{\cdot-}$ contribute to the absorption.

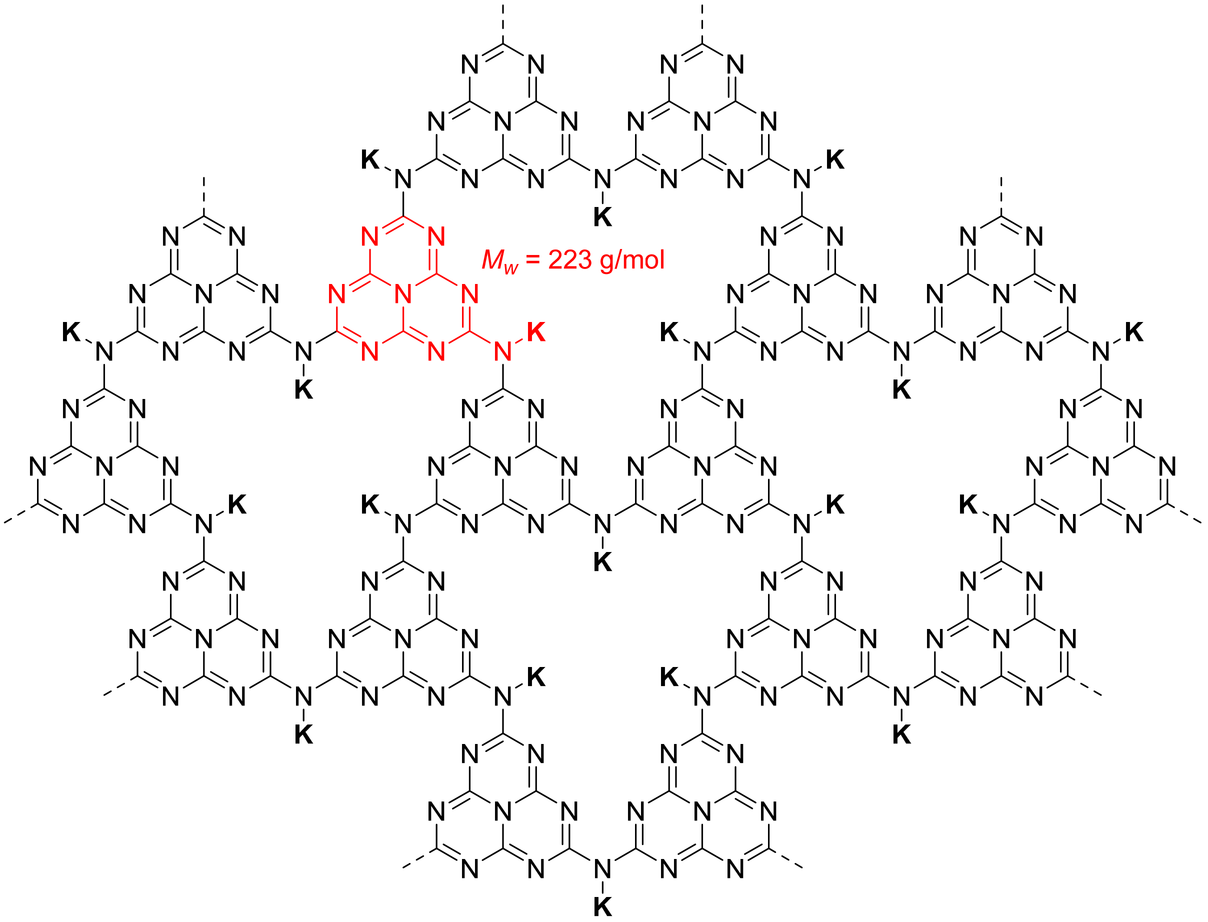


Fig. S5. Ideal structure of K-PHI.

A procedure of K-PHI radical anion quenching with AgOTf

A screw-capped tube (5 mL) was charged with benzylamine (0.2 mmol), K-PHI (5 mg), MeCN (3 mL) and magnetic stir bar. The mixture was degassed using freeze-pump-thaw method (3 times, liquid nitrogen, residual pressure $7\cdot10^{-5}$ bar) and refilled with CO_2. Four tubes were prepared using the same amount of the reagents. The mixture was stirred at 35°C under blue LED irradiation (λ_{max} = 461 nm, $0.0517\pm3\cdot10^{-5}$ $mW\cdot cm^{-2}$) for 72h. The tubes were transferred into the glove box (residual O_2 concentration <0.1 ppm, residual H_2O concentration <0.1 ppm). Reaction mixtures of dark green color from four tubes were combined in a 50 mL Schlenk flask. Schlenk flask was covered with a rubber septum and removed from the glove box. A freshly prepared solution of silver(I) triflate in deoxygenated water (17.6 mL, 0.0681 $mol\cdot L^{-1}$) was injected through the septum into the Schlenk flask. Suspension immediately changed color from green to black. The solid was separated by centrifugation (13000 rpm, 5 min), washed with water, acetonitrile and ethanol. The solutions were combined and concentrated in vacuum (50°C, 20 mbar). The resulting residue was washed with benzene, dried in vacuum (50°C, 20 mbar) and was identified as benzylammonium triflate.

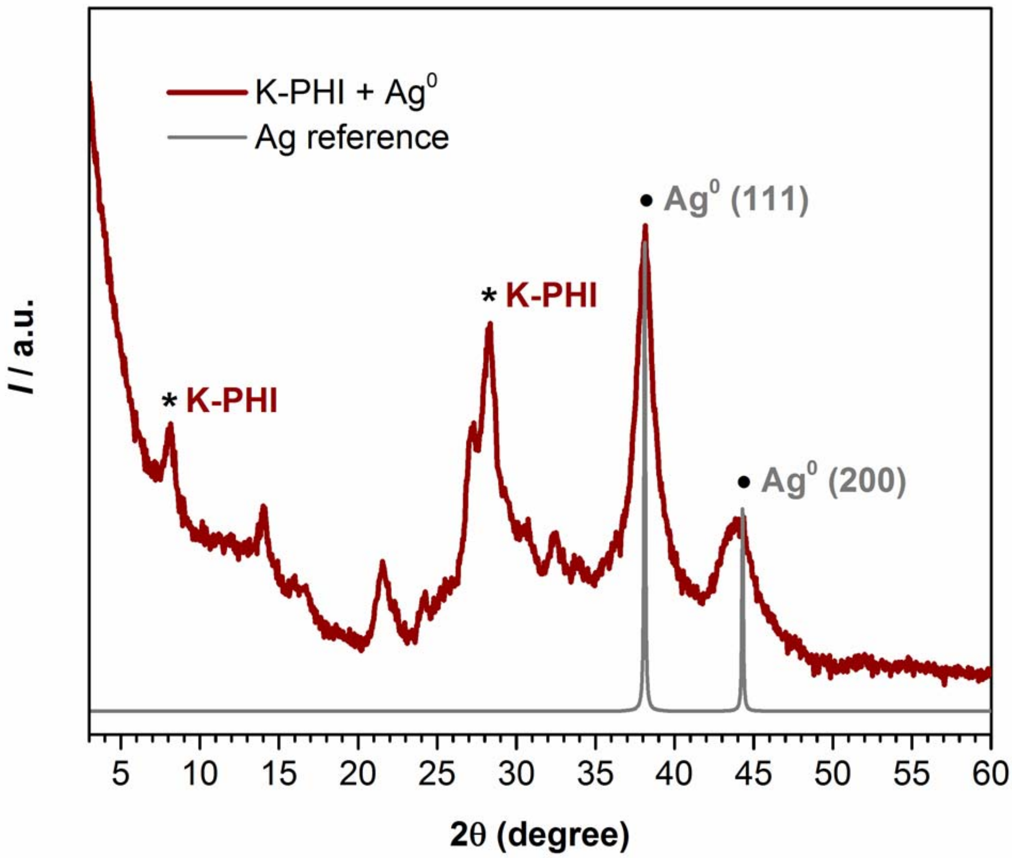


Fig. S6. PXRD pattern of Ag@KPHI generated upon K-PHI$^{\cdot-}$ quenching with AgOTf. Reference X-Ray diffraction pattern of Ag^0 taken from the literature.[4]

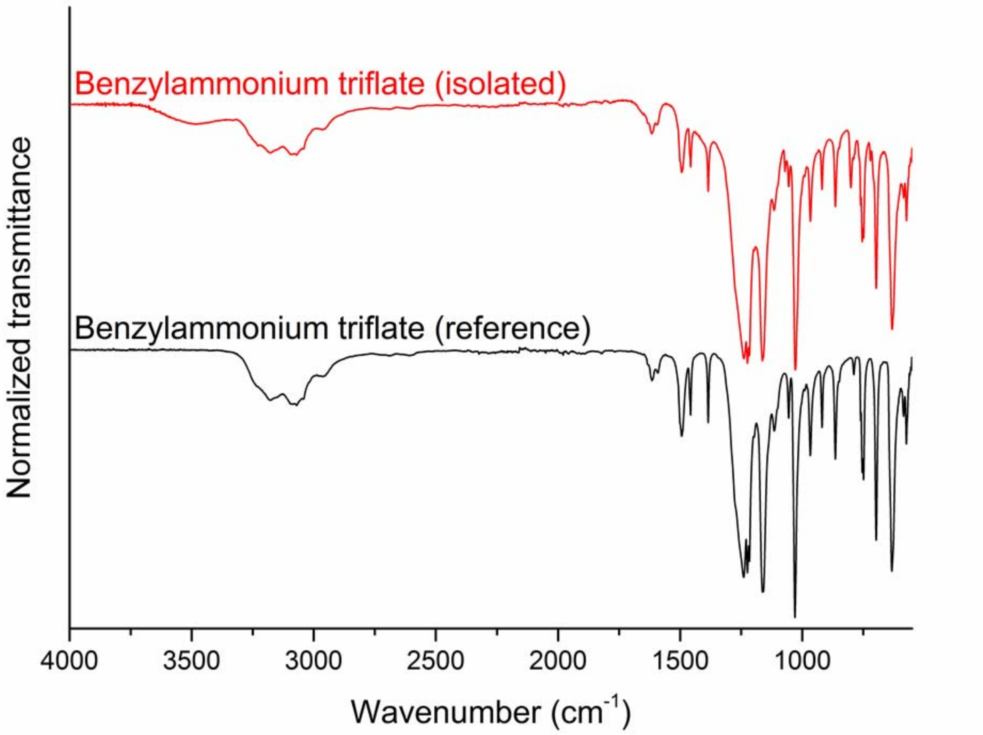


Fig. S7. FT-IR spectra of benzylammonium triflate isolated upon K-PHI$^{\bullet-}$ quenching with AgOTf (red, top) and prepared by neutralization of benzylamine with HOTf (black, bottom).

Preparation of (^{15}N)benzylcarbamic acid

An NMR tube was charged with (^{15}N)benzylamine (5 µL), CD$_3$CN (0.4 mL) and DMSO-*d*$_6$ (0.1 mL). CO$_2$ was bubbled through the solution for 1 minute. ^{1}H NMR (400 MHz, Acetonitrile-*d*$_3$) δ 7.26 (ddt, *J* = 21.2, 13.9, 7.2 Hz, 5H), 6.69 (dt, *J* = 92.1, 6.2 Hz, 1H), 4.18 (d, *J* = 5.9 Hz, 2H). ^{13}C NMR (101 MHz, Acetonitrile-*d*$_3$) δ 158.59 (d, *J* = 24.8 Hz), 141.19, 129.04, 127.74, 127.45, 125.40, 44.69 (d, *J* = 11.6 Hz). ^{15}N NMR (41 MHz, Acetonitrile-*d*$_3$) δ 83.49 (d, *J* = 92.3 Hz).

Preparation of benzylcarbamic acid

CO$_2$ was passed through a solution of benzylamine (80 µL) in MeCN (5 mL). White precipitate was filtered of and washed briefly with MeCN. Yield: 41%.

Degradation of benzylcarbamic acid

A screw-capped tube (5 mL) was charged with benzylcarbamic acid (0.05 mmol), K-PHI (5 mg), MeCN (3 mL) and magnetic stir bar. The mixture was degassed using freeze-pump-thaw method (3 times, liquid nitrogen, residual pressure $7\cdot10^{-5}$ bar) and refilled with CO$_2$. The mixture was stirred at 35°C under blue LED irradiation (λ_{max} = 461 nm, $0.0517\pm3\cdot10^{-5}$ mW·cm^{-2}) for 24h. Catalyst was separated by centrifugation. An aliquot (0.3 mL) of the MeCN solution was transferred into the NMR tube, CD$_3$CN (0.3 mL) and CH$_2$Cl$_4$ (0.5 µL) as an internal standard were added to the NMR tube.

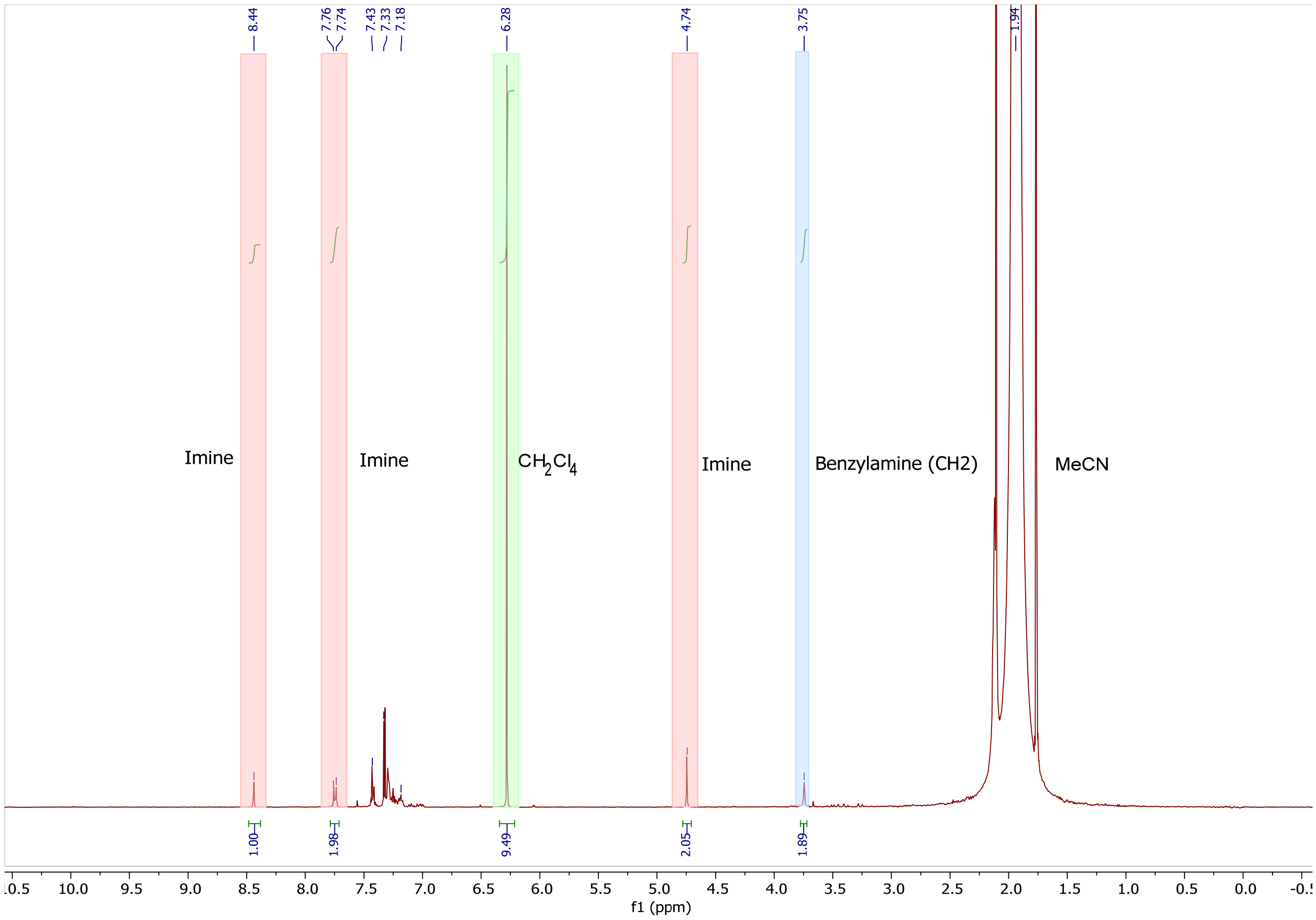


Fig. S8. ^{1}H NMR spectra of the reaction mixture obtained using benzylcarbamic acid as an electron donor in IDEAS experiment. Characteristic proton peaks of imine, benzylamine and internal standard in the ^{1}H NMR spectrum are labeled.

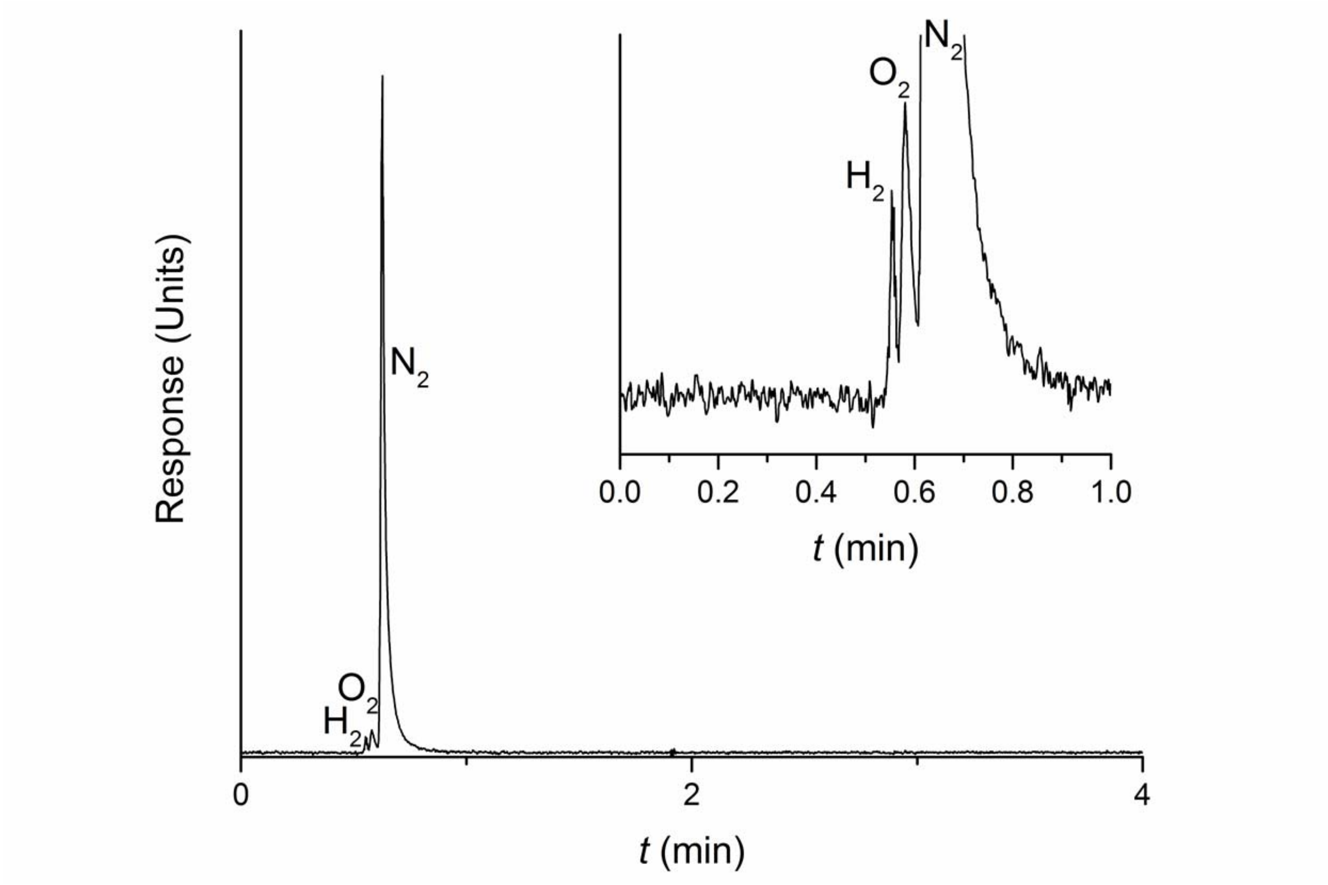
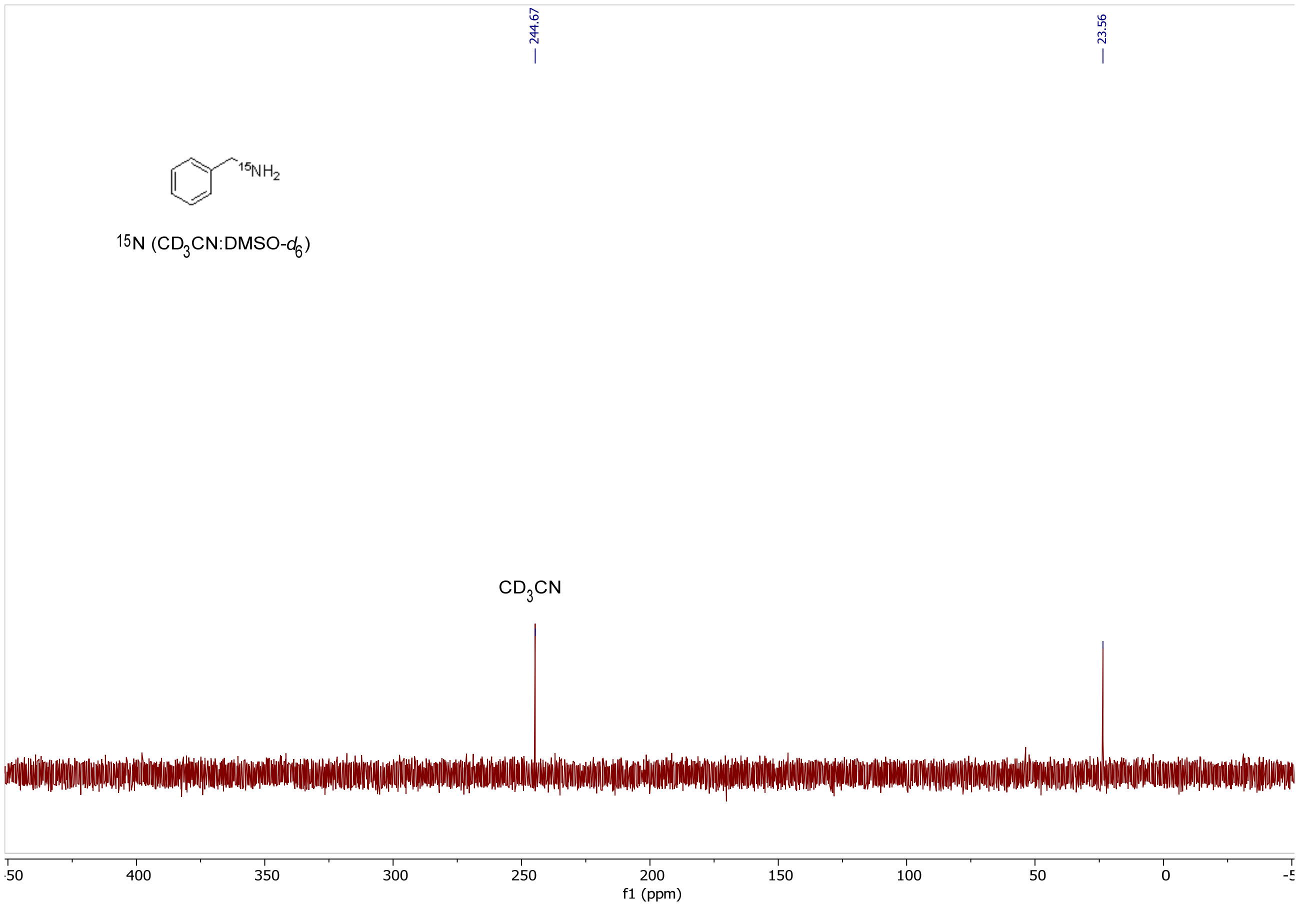
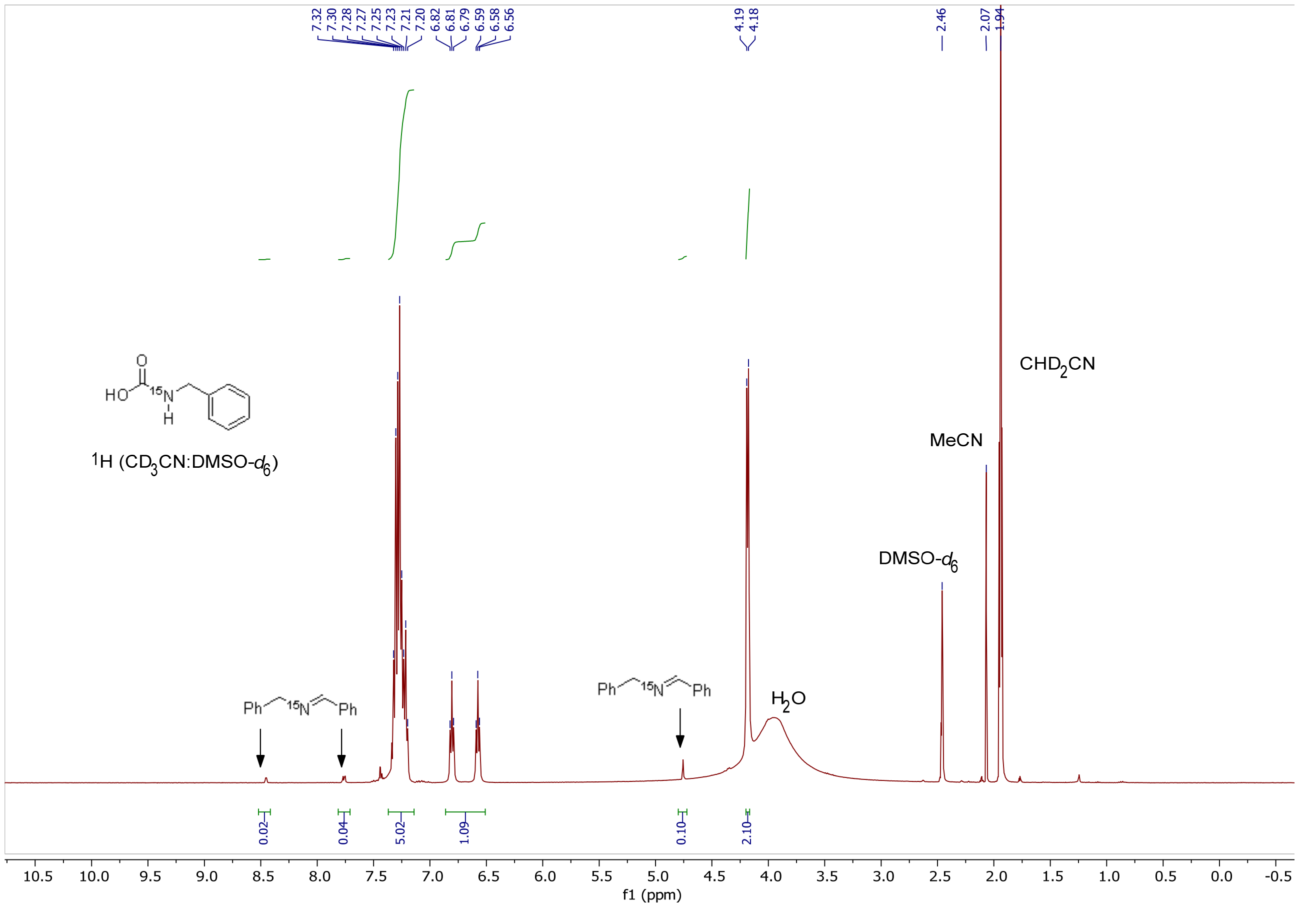
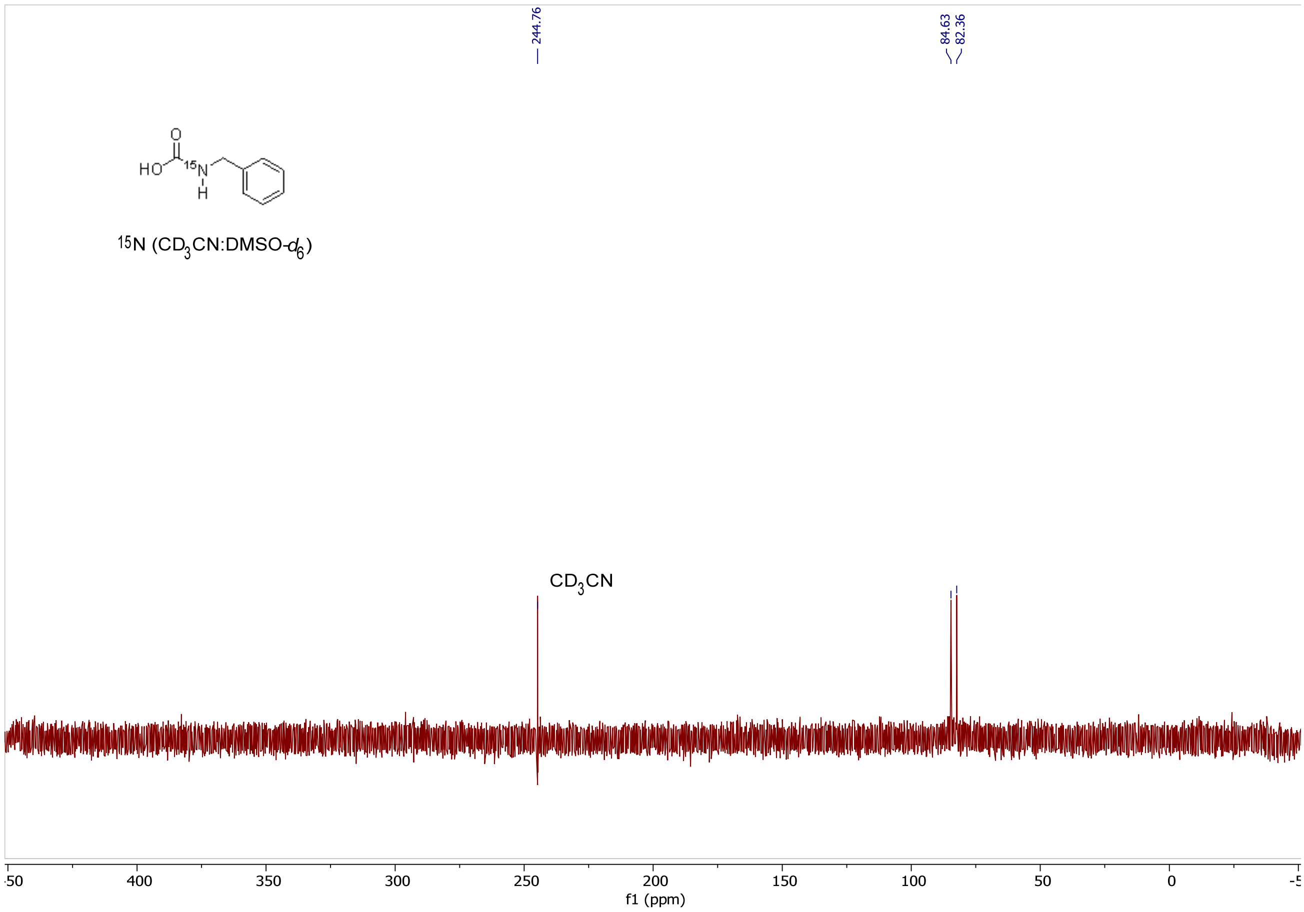


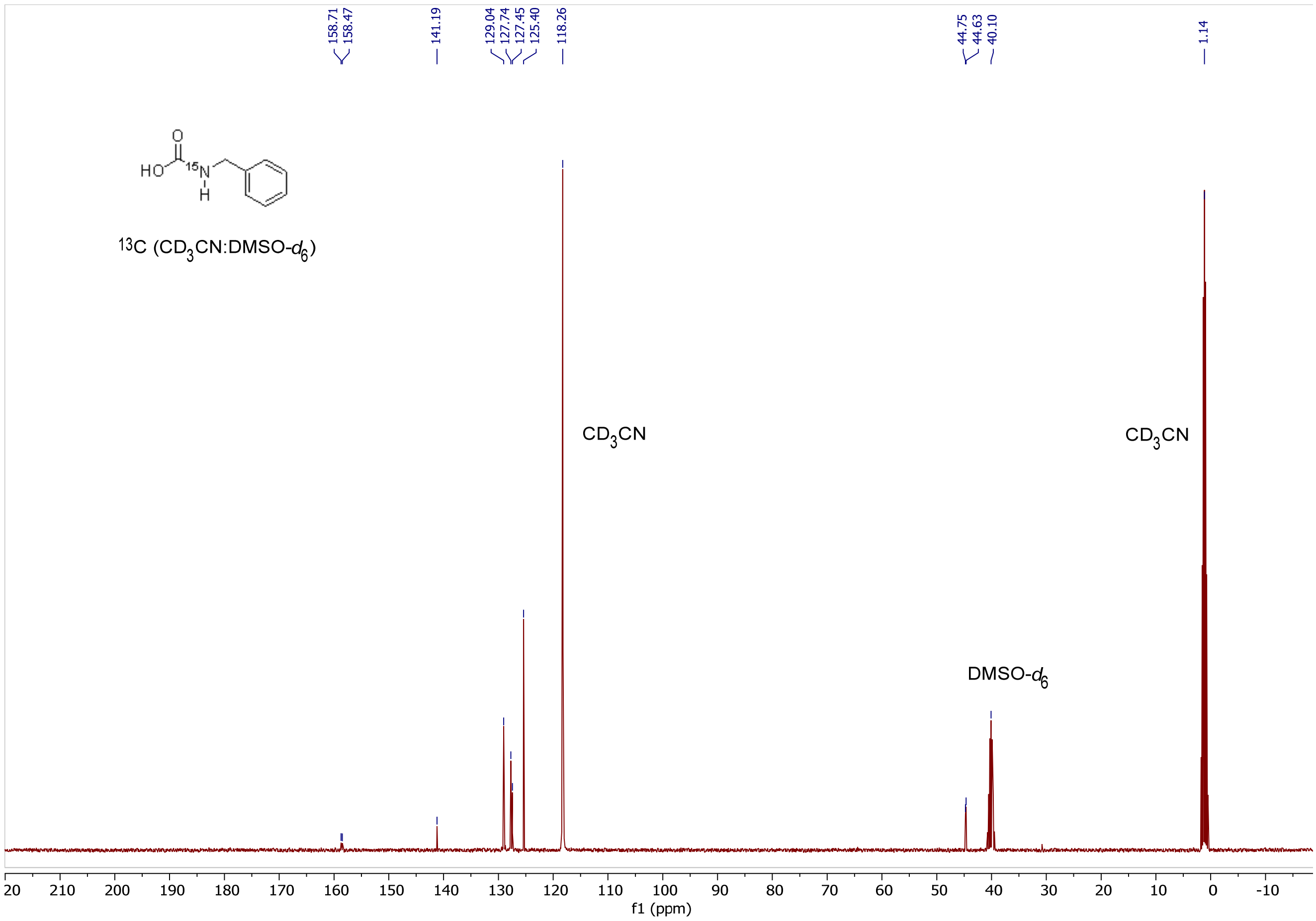
Fig. S9. GC-TCD of the reaction mixture head space. The peaks of N_2 and O_2 are due to imperfect connection between the syringe barrel and a plunge during transfer the reaction mixture head space from the reactor to gas chromatograph. The amount of H_2 quantified in this experiment was 1.48 nmol.

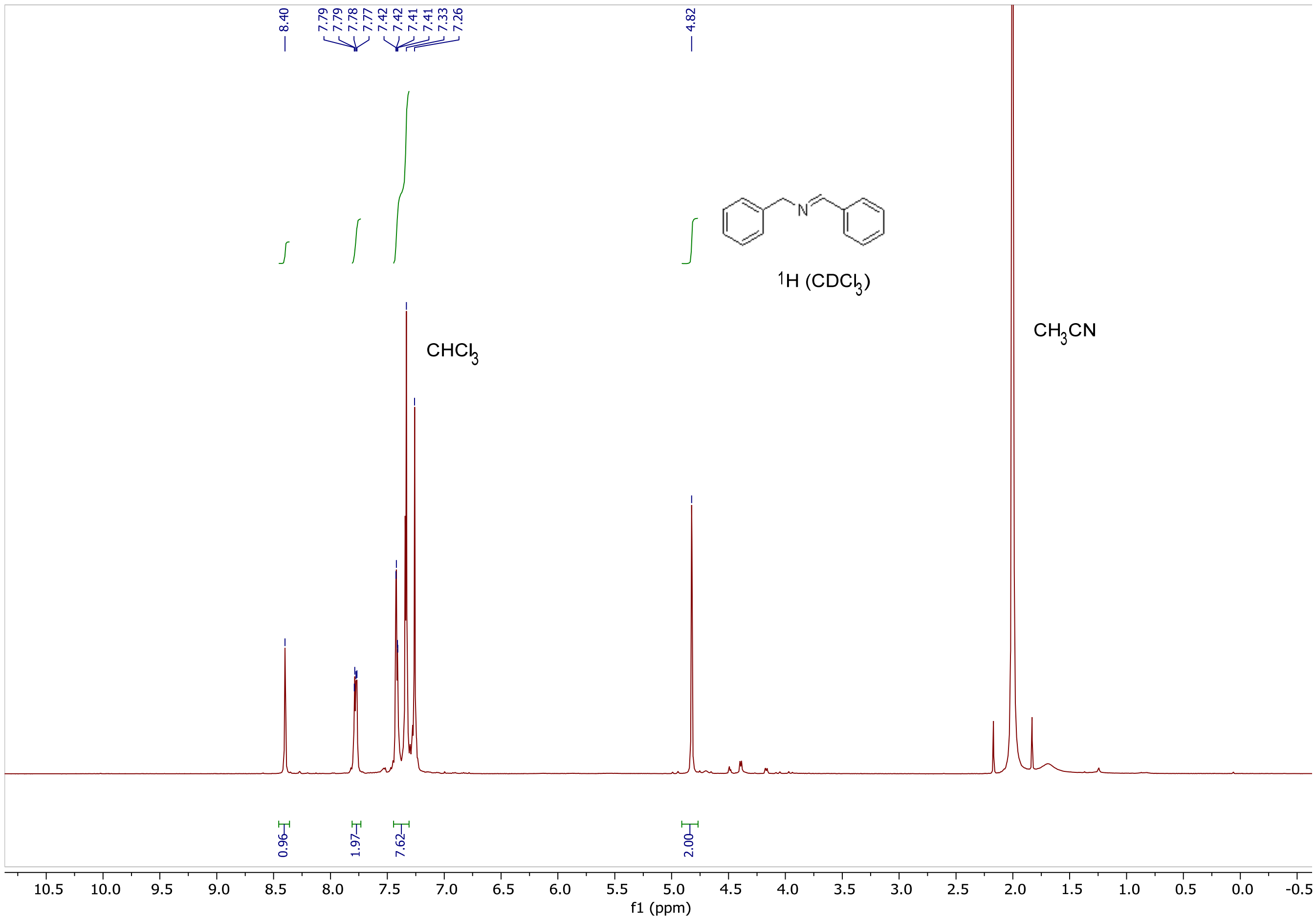
NMR spectra


244.67
23.56
15NH2
15N (CD3CN:DMSO-d6)
CD3CN
50
400
350
300
250
200
150
100
50
0
-5
f1 (ppm)


7.32
7.30
7.28
7.27
7.25
7.23
7.21
7.20
6.82
6.81
6.79
6.59
6.58
6.56
4.19
4.18
2.46
2.07
1.94
O
HO
15N
H
1H (CD3CN:DMSO-d6)
CHD2CN
MeCN
DMSO-d6
H2O
Ph
15N
Ph
Ph
15N
Ph
0.02
0.04
5.02
1.09
0.10
2.10
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


244.76
84.63
82.36
HO
O
15N
H
15N (CD3CN:DMSO-d6)
CD3CN
50
400
350
300
250
200
150
100
50
0
-5
f1 (ppm)


158.71
158.47
141.19
129.04
127.74
127.45
125.40
118.26
44.75
44.63
40.10
1.14
HO
O
15N
H
13C (CD3CN:DMSO-d6)
CD3CN
CD3CN
DMSO-d6
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



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