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Ionic Liquid and Conjugated Polymer

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Visible-Light-Driven Conversion of CO₂ from Air to CO Using an

A metal-free and highly efficient catalytic system involving a taskspecific ionic liquid, $[P_{4444}][p-2-O]$, and a pyrene-based conjugated polymer was developed for direct CO₂ capture from air and further photoreduction to CO under visible light irradiation, affording a CO production rate of 47.37 µmol g⁻¹ h⁻¹ with a selectivity of 98.3%.

Since industry revolution, the CO₂ concentration in air increases continuously and reaches ~400 ppm nowadays, which has destroyed the natural balance of carbon cycling and caused serious environmental problems. Therefore, the CO2 issue has been paid much attention across the world.¹⁻⁴ CO₂ capture from air⁵⁻⁸ and further transformation into fuels and chemicals⁹ are efficient ways to reduce CO₂ concentration in air, which may provide a good supplement to the natural carbon cycling. In natural photosynthesis, the capture of CO₂ from air followed by further conversion is achieved in plants under sunlight irradiation. To mimic natural photosynthesis, the catalytic system that can capture CO₂ from air and simultaneously photocatalyze its conversion is highly required. As known, water involves in natural photosynthesis. If water together with CO₂ can be captured from air and photoconverted into chemicals or fuels, it would be very interesting.

To date, various photocatalysts including inorganic and inorganic/organic hybrid semiconductors have been developed for CO_2 photoreduction to fuels or chemicals (e.g., CO, HCOOH, methanol, CH₄, etc.).¹⁰⁻¹⁴ However, most of the reported photocatalysts are metal-based, and metal-free photocatalysts or catalytic systems are seldom reported.¹⁵⁻¹⁷ In recent years, conjugated polymers (CPs) have emerged as a kind of designable and metal-free materials, which can be prepared

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via polymerization of functional monomers,¹⁸⁻²⁰ showing promising potentials in photocatalysis. For example, pyrenebased CPs have been found to show high efficiency for photoproduction of H₂ from H₂O under visible light illumination.²¹⁻²³ However, CPs have not been applied in the photoconversion of CO₂ in a literature survey to date.

Ionic liquids (ILs), entirely composing of ions, possess unique properties such as negligible vapor pressure, wide liquid and electrochemical windows, good solvent power for organics/inorganics, etc. Importantly, they can be designed with specific functions via choice of cations and anions, thus have been widely applied in many areas.²⁴⁻²⁸ Especially, CO₂reactive ILs including azolate-, alcoholate-, phenolate-, amino acid-containing anion- and pyridine-containing anion-based ILs, ^{27,28} have been demonstrated to be capable of efficiently capturing CO₂ under ambient conditions, which provide the possibility to capture CO₂ from air. Many ILs are apt to absorb H_2O via hydrogen bonding.^{29,30} If ILs are designed to have the ability to simultaneously capture CO₂ and H₂O from air, they may promote the CO₂ photoreduction in the presence of appropriate photocatalysts.



Scheme 1. (a) Yamamoto reaction to synthesize the the representative CPs (i.e., CP1) via the reaction of the tetrabromopyrene monomer with the other monomer (i.e., 1,4-dibromobenzene); (b) chemical structures of the monomers of CP2 to CP5 from left to right; (c) the statistical structures of the as-synthesized CPs.

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Electronic Supplementary Information (ESI) available: procedure to prepare the pyrene-based CPs, characterization of CPs, procedure to photoreduction of CO_2 , analysis on the products of CO_2 photoreduction by GC and GC-MS, etc. See DOI: 10.1039/x0xx00000x

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Herein, we report a robust and metal-free catalytic system involving a task-specific IL, $\left[P_{4444}\right]\left[p\text{-}2\text{-}O\right]$ (Figure 1a), and a pyrene-based CP for one-pot CO₂ capture and conversion to CO under visible light irradiation. The IL could capture CO₂ chemically and absorb H_2O via hydrogen bonding from air, further activating them confirmed by the DFT calculation. The as-prepared pyrene-based CPs shown in Scheme 1 exhibited conduction bands (CBs) from -0.78 to -1.52 eV, lower than the redox potential of CO₂ reduction to CO. The pyrene-based CP in combination with the IL realized the capture of CO₂ from air and further photoreduction to CO under visible light irradiation, affording a CO production rate up to 47.37 μ mol g⁻¹ h⁻¹ with a high selectivity of 98.3%. Moreover, it was demonstrated that the IL enhanced the CO₂ photoreduction to CO and suppressed H₂ evolution. To the best of our knowledge, this is the first example to realize the direct capture of CO₂ and H₂O from air and transformation to CO by a metal-free catalytic system under visible light irradiation.

Five pyrene-based CPs as illustrated in Scheme 1 were synthesized using the nickel-catalyzed Yamamoto protocol (Figure S1).³¹ FT-IR and Solid ¹³C NMR analysis confirmed the formation of these CPs (Figures S2 and S3). All the resultant polymers were insoluble in common solvents, displaying irregular morphology (Figures S4) with crystalline structures confirmed by powder X-ray diffraction (Figure S5). Thermogravimetric analysis indicated that the polymers were thermally stable in nitrogen up to 300 °C (Figure S6). The UV/vis diffuse reflectance spectra of the polymers are displayed in Figure S7, from which the energy gaps (Eg) were obtained as listed in Table 1. The valence band (VB) of the resultant CPs was obtained from the XPS spectra, and thus the conduction band (CB) was estimated based on the formula: CB= VB-Eg. It is clear that these CPs showed lower CBs than the redox potential of CO₂ reduction to CO.³²

The IL, [P₄₄₄₄][p-2-O] (Figure 1a), was reported to be capable of efficiently absorbing CO₂ under ambient conditions.²⁷ Here it was found that this IL could simultaneously capture CO₂ and H₂O from air, confirmed by the ¹H and ¹³C NMR analysis (Figure S8). The new signal at 4.06 ppm in the ¹H NMR spectrum of the IL treated with air was ascribed to the H of the absorbed H₂O (Figure 1c), and the new peak at 160.06 ppm in the ¹³C NMR spectrum was assigned to the C atom of the absorbed CO₂ via forming the IL-CO₂ complex at the interaction site of aryl O according to the previous report (Figure 1d).²⁷ The mass gain of the IL treated with air increased rapidly with time and

Table 1.	Properties	of conjugated	polymers	(CPs) ¹	
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Conjugated	Eg	VB	СВ	λ_{em}
Polymer	/ eV ^[a]	/ eV ^[b]	/ eV ^[c]	/ nm ^[d]
CP1	2.48	1.70	-0.78	423.2
CP2	2.17	1.26	-0.91	422.2
CP3	2.86	1.40	-1.46	422.4
CP4	2.76	1.61	-1.15	423.8
CP5	2.66	1.14	-1.52	421.4

 $^{[a]}$ Energy gap, Eg, derived from the solid UV-vis absorption spectra. $^{[b]}$ Valence band, VB, derived from XPS. $^{[c]}$ Conduction band, CB= VB-Eg. $^{[d]}$ The maximum peak of fluorescence spectra excited at 360 nm.



Figure 1. (a) Chemical structure of the IL used; (b) Mass gain of the IL as a function of time. The inset is the mass ratio of absorbed CO_2 and H_2O for 48 h. (c); ¹H and (d)¹³C NMR spectra of IL before and after capturing CO₂ and H_2O from air for 48 h

reached 350 mg per g IL after 12 h (Figure 1b), while prolonging time to 48h, it increased little. This indicates that the IL could rapidly and efficiently capture CO_2 and H_2O from air. The amount of CO₂ was roughly estimated based on the ¹³C NMR spectrum as suggested by Olah,⁹ which was ~33 mg CO₂ per g IL (9.3 wt%). This value was much lower than the CO₂ absorption capacity by this IL (i.e., 180 mg/g)²⁷ under waterfree and pure CO₂ atmosphere, probably due to the interruption of highly-absorbed H₂O (90.7 wt%). It suggests that CO_2 could be captured and further may be activated by the IL in the presence of H_2O . It is worth pointing out that the IL could be regenerated and reused to uptake CO₂ from air for at least five times (Figure S9).



Figure 2. Interaction parameters of IL-H₂O (a) and IL-CO₂ (b) via O site and N site of IL calculated by DFT b3lyp/6-31++G(d, p) method. These interaction parameters include bond length, bond angle, and interaction enthalpy. O (red), N (blue), C (grey), H (white).

The information on the bond length and bond angle of the absorbed H₂O and CO₂ by the IL gave more interesting results (Figure 2 and Table S1). Specifically, optimized IL-CO₂ bond lengths at N site (L_{N-C} 1.622 Å) or O site (L_{O-C} 1.587 Å) were shorter than those of IL-H₂O (i.e., L_{N-H} 2.245 Å and L_{O-H} 1.731 Å), respectively (Figures 2a and 2b). It means that CO₂ was closer to the interaction site than H_2O , thus probably favoring to

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being activated by the IL. The activation of CO_2 and H_2O by the IL could be evaluated by their bond angle change after being attracted by the IL. As illustrated in Figure 2, the bond angle of CO_2 changed considerably from 180 to 137.80 or 136.79° after captured by the IL, while the bond angle of H_2O changed slightly from 104.5 to 102.13° or 97.13°. The bond angle change of CO_2 might be caused by the formation of carbonate and carbamate via the reactions of CO_2 with phenolate at the O and N sites, while that of H_2O may be ascribed to the hydrogen bonding. From these results, it seems that the IL activates CO_2 more strongly than H_2O in spite of higher H_2O absorption capacity than that of CO_2 from air by IL, which may be favorable to the CO_2 photoreduction as discussed below.

Table 2. Visible-light photoreduction of absorbed CO_2 from air by ILs by using conjugated polymers (CPs) as photocatalysts.^[a]

Entr	Catalyst	Medium	Gas Type	Produrate/	uction µmolg ⁻¹	Sel./ %
				H_2	со	со
1	CP1	[P ₄₄₄₄][p-2-O]	Air	5.90	14.53	71.1
2	CP2	[P ₄₄₄₄][p-2-O]	Air	1.16	27.45	95.9
3	CP3	[P ₄₄₄₄][p-2-O]	Air	1.20	41.44	97.2
4	CP4	[P ₄₄₄₄][p-2-O]	Air	1.16	31.76	96.5
5	CP5	[P ₄₄₄₄][p-2-O]	Air	0.81	47.37	98.3
6	CP5	[P ₄₄₄₄][p-2-O]	Ar	0.44	$ND^{[b]}$	_[c]
7	CP5	[P ₄₄₄₄][p-2-O]	CO_2	0.63	48.98	98.7
8	CP5	0.5 M NaHCO ₃	Air	4.28	trace	_
9	CP5	0.5 M NaHCO ₃	CO ₂	1.20	8.72	87.9
10	Hexagon al C_3N_4	Water vapor	CO ₂	_	1.83	33 ¹⁷
11	$C_3N_4/$ carbon	Water vapor	CO ₂	_	ca. 3.0	15

 $^{[a]}$ Reaction conditions: CP, 50 mg; IL treated with air for 48h, 10 g; TEOA, 1 g; visible light > 420 nm. The data from references were all obtained under visible light irradiation and the corresponding cited photocatalysts are also all-organic polymers without any metal species. $^{[b]}$ ND means "not detectable". $^{[c]}$ — means not available.

Based on the above results, using the IL as the CO₂ and H₂O absorbent from air and the resultant CPs as the catalyst, the photocatalytic experiments were carried out in the IL with a sacrificial electrondonor triethanolamine (TEOA) under visible light illumination (λ >420 nm, Table 2). Before the photocatalytic experiment, the IL was bubbled with air for 48h, which was used as the CO_2 and H_2O resources for the photocatalytic experiment (see Supporting Information). The blank experiments showed that no reaction occurred in dark or without the CP catalyst. To our delight, using the CPs as the catalyst and the air-treated-IL as the reaction medium, CO was obtained as the sole carbonaceous compound under the visible light irradiation and air atmosphere (Figure S10). All the CPs showed good photocatalytic activity, affording CO with the production rates following the order: CP5>CP3>CP4>CP2>CP1 (Table 2, entries 1-5). This order was identical to that of the CB values of the CPs (Table 1), suggesting that the activity of the photocatalyst was related to its CB. CP5 with the most negative CB value (-1.52 eV) showed the best performance with a CO production rate of 47.37 μ mol g⁻¹ h⁻¹, which was a high value of CO production compared to those obtained by the reported photocatalytic systems,³⁴ and much higher than the highest value obtained over the metal-free catalytic system reported to date (Table 2).^{15,17} The activity of the CPs may also be related to its photocurrent. CP5 displayed the largest photocurrent (Figure S11), suggesting the strong ability to photogenerate electrons irradiated by the visible light, which was favorable to the photoreduction of CO₂.

To explore the origin of CO, a control experiment was performed under Ar atmosphere, and no CO was detected (Table 2, entry 6). Using isotope $^{13}\text{CO}_2$ instead of CO_2 for photoreduction, ¹³CO was obtained under the same other conditions, confirmed by GC-MS analysis (Figures S12, S13). All these findings indicate that the production of CO resulted from the photoreduction of CO₂ under the experimental conditions. For comparison, the photocatalytic reaction was performed under the pure CO₂ atmosphere, and CO was produced with a slightly higher rate than that obtained under the air atmosphere (Table 2, entries 7 vs 5). This suggests that the released IL in the reaction process could further capture free CO₂ molecules, thus affording more CO. Using the NaHCO₃ aqueous solution as the reaction medium, the photocatalytic reaction was performed. Trace amount of CO was detected under air atmosphere, while CO with production rate of 8.72µmolg⁻¹h⁻¹ was obtained under the CO₂ atmosphere (Table 2, entries 8 and 9). These results suggest that besides capturing CO₂ from air the IL maybe also promoted the photoreduction of CO₂.

The Gaussian calculation showed that the IL could activate CO_2 , and the IL- CO_2 interaction via both N site and O site were thermodynamically favorable. Therefore, the attracted CO_2 by the IL was more favorable to be photoreduced compared to free CO_2 molecule. In addition, the calculated \triangle G values of IL-CO interaction via both N site (236.78 KJ/mol) and O site (2.28 KJ/mol) were positive (Figure S14), indicating that the IL was difficult to bind with CO. That is, the generated CO from CO_2 photoreduction could be easily released from the catalytic system, thus faciliating the IL to capture CO_2 again.

It was reported that pyrene-based CPs was efficient for the photocatalytic production of H₂ from H₂O under visible-light irradiation.²¹⁻²³ In this work, the H₂ evolution was also observed using the resultant pyrene-based CPs as the catalysts. Interestingly, the H₂ evolution was effectively suppressed by the IL in the CO₂ photoreduction process compared to the case of using the NaHCO₃ reaction medium under the similar conditions (Table 2, entries 7 vs 9). This indicates that the IL could improve the selectivity to CO in the CO₂ photoreduciton process. Similar phenomenon was reported by Wang and coworkers, who found that the conventional ILs (e.g., 1-ethyl-3-methylimidazolium tetrafluoroborate) could enhance the CO evolution from photoreduction of CO₂ using an metal-containing photocatalyst.¹⁶

The stability and reusability of the IL-CP5 system were examined. After one run, the IL-CP5 reaction system was degassed for 2h, and then treated with air for capturing CO_2

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and H_2O again, which was then reused for the next run. It was indicated that the reaction system still worked well after reused for 5 times, as shown in Figure S15a. Moreover, the kinetic study demonstrated that the catalyst was reusable with similar activity (Figure S15b). In addition, the IL was examined by ^{13}C NMR analysis after visible-light irradiation, and the recovered IL still kept its original chemical structure (Figure S8), suggesting that the IL was tolerable to the light irradiation under the experimental conditions. The CP5 catalyst reused for 5 times was examined by XRD, and it had the same XRD pattern as the fresh catalyst (Figure S15c). The above results indicate that the IL-CP5 catalytic system was stable and reusable.

The above results indicate that the combination of the IL and the resultant CPs achieved the direct capture of CO₂ from air and further conversion to CO. Based on the experimental results, we propose a possible mechanism for the capture of CO₂ from air and further photoreduction to CO as illustrated in Scheme 2 and Scheme S1. CO₂ and H₂O molecules are captured from air and activated by the IL. Upon the visible light illumination on the CP catalyst, the photo-generated electrons transfer from the VB to the CB of the CP catalyst, leaving the holes on the VB. The photoinduced holes in the VB may oxidize the sacrifice reagent TEOA. Meanwhile, the photogenerated electrons in the CB may react with the IL-activated CO₂ molecules to form CO_2^{-1} . Then CO_2^{-1} reacts with H⁺ proton from H₂O and the photogenerated electron to form CO. As known, the reduction of CO₂ to CO involves a 2-electron process. Once CO is formed, the IL is regenerated due to the easy release of CO as discussed above, which can be used to capture CO₂ or H₂O molecules again.



Scheme 2. Proposed CO₂ photoreduction mechanism by using CP as metal-free photocatalyst and IL-absorbed CO₂/H₂O from air as raw material under visible-light irradiation.

In summary, a metal-free and highly efficient catalytic system involving a task-specific IL, $[P_{4444}]$ [p-2-O], and a pyrenebased CP was developed for the direct capture of CO₂ from air and further photoreduction to CO under visible light irradiation. A high CO production rate of 47.37 µmol g⁻¹ h⁻¹ was achieved with a high selectivity of 98.3%. Moreover, it was demonstrated that the IL enhanced the CO₂ photoreduction to CO and suppressed H₂ evolution. This work may open up a new way to direct capture and photo-driven conversion of CO₂ from air into chemical and fuels.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

- W. J. Ong, L. L. Tan, Y. H. Ng, S. T. Yong, S. P. Chai, *Chem. Rev.* 2016, **116**, 7159.
- 2 G. A. Olah, G. K. S. Prakash, A. Goeppert, J. Am. Chem. Soc. 2011, **133**, 12881.
- 3 M. Y. He, Y. H. Sun, B. X. Han, Angew. Chem. Int. Ed. 2013, 52, 9620.
- 4 F. Julia-Hernandez, T. Moragas, J. Cornella, R. Martin, *Nature*, **2017**, 545(7652), 84.
- 5 E. S. Sanz-Perez, C. R. Murdock, S. A. Didas, C. W. Jones, *Chem. Rev.* 2016, **116**, 11840.
- 6 T. M. McDonald, W. R. Lee, J. A. Mason, B. M. Wiers, C. S. Hong, J. R. Long, J. Am. Chem. Soc. 2012, **134**, 7056.
- 7 A. Goeppert, M. Czaun, R. B. May, G. K. S. Prakash, G. A. Olah, S. R. Narayanan, J. Am. Chem. Soc. 2011, 133, 20164.
- 8 X. Y. Shi, H. Xiao, K. S. Lackner, X. Chen, *Angew. Chem. Int.* Ed. 2016, **55**, 4026.
- 9 a) J. Kothandaraman, A. Goeppert, M. Czaun, G. A. Olah, G. K. S. Prakash, J. Am. Chem. Soc. 2016, 138, 778; b) J. Kothandaraman, A. Goeppert, M. Czaun, G. A. Olah, G. K. S. Prakash, Green Chem. 2016, 18, 5831; c) Y. N. Li, L. N. He, A. H. Liu, X. D. Lang, Z. Z. Yang, B. Yu, C. R. Luan, Green Chem. 2013, 15, 2825.
- R. Kuriki, H. Matsunaga, T. Nakashima, K. Wada, A. Yamakata, O. Ishitani, K. Maeda, J. Am. Chem. Soc. 2016, 138, 5159.
- 11 H. Takeda, K. Ohashi, A. Sekine, O. Ishitani, J. Am. Chem. Soc. 2016, **138**, 4354.
- 12 T. Kajiwara, M. Fujii, M. Tsujimoto, K. Kobayashi, M. Higuchi, K.Tanaka, S. Kitagawa, Angew. Chem. Int. Ed. 2016, 55, 2697.
- H.-Q. Xu, J. Hu, D. Wang, Z. Li, Q. Zhang, Y. Luo, S.-H. Yu, H.-L. Jiang, J. Am. Chem. Soc. 2015, 137, 13440.
- 14 D. Won, J. Lee, J. Ji, W. Jung, H. Son, C. Pac, S. O. Kang, J. Am. Chem. Soc. 2015, 137, 13679.
- 15 Y. Wang, X. Bai, H. Qin, F. Wang, Y. Li, X. Li, S. Kang, Y. Zuo, L. Cui, Acs. Appl. Mater. Inter. 2016, 8, 17212.
- 16 J. L. Lin, Z. X. Ding, Y. D. Hou, X. C. Wang, *Sci. Rep.* **2013**, *3*, 1056.
- 17 Z. Q. He, D. F. Wang, J. T. Tang, S. Song, J. M. Chen, X. Y. Tao, *Environ. Sci. Pollut. R.* 2017, 24, 8219.
- 18 G. Ji, Z. Yang, H. Zhang, Y. Zhao, B. Yu, Z. Ma, Z. Liu, Angew. Chem. Int. Ed. 2016, 55, 9794.
- C. Gu, N. Huang, Y. C. Chen, L. Q. Qin, H. Xu, S. T. Zhang, F. H. Li, Y. G. Ma, D. L. Jiang, *Angew. Chem. Int. Ed.* 2015, 54, 13594.
- 20 Y. H. Xu, S. B. Jin, H. Xu, A. Nagai, D. L. Jiang, Chem. Soc. Rev. 2013, 42, 8012.
- 21 G. Zhang, Z. Lan, X. Wang, Angew. Chem. Int. Ed. 2016, 55, 15712.
- 22 L. Li, Z. Cai, Q. Wu, W. Lo, N. Zhang, L. X. Chen, L. Yu, J. Am. Chem. Soc. 2016, **138**, 7681.
- 23 R. S. Sprick, J. Jiang, B. Bonillo, S. Ren, T. Ratvijitvech, P. Guiglion, M. A. Zwijnenburg, D. J. Adams, A. I. Cooper, J. Am. Chem. Soc. 2015, 137, 3265.

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Journal Name

- 24 B. A. Rosen, A. Salehi-Khojin, M. R. Thorson, W. Zhu, D. T. Whipple, P. J. A. Kenis, R. I. Masel, *Science* 2011, **334**, 643.
- 25 Y. F. Zhao, B. Yu, Z. Z. Yang, H. Y. Zhang, L. D. Hao, X. Gao, Z. M. Liu, Angew. Chem. Int. Ed. 2014, 53, 5922.
- 26 K. Chen, G. Shi, W. Zhang, H. Li, C. Wang, J. Am. Chem. Soc. 2016, **138**, 14198.
- 27 X. Y. Luo, Y. Guo, F. Ding, H. Q. Zhao, G. K. Cui, H. R. Li, C. M. Wang, *Angew. Chem. Int. Ed.* 2014, **53**, 7053.
- 28 C. M. Wang, X. Y. Luo, H. M. Luo, D. E. Jiang, H. R. Li, S. Dai, Angew. Chem. Int. Ed. 2011, 50, 4918.
- 29 Y. Chen, X. F. Sun, C. Y. Yan, Y. Y. Cao, T. C. Mu, J. Phys. Chem. B 2014, 118, 11523.
- 30 Y. Chen, Y. Y. Cao, C. Y. Yan, Y. W. Zhang, T. C. Mu, J. Phys. Chem. B 2014, 118, 6896.
- 31 J. X. Jiang, A. Trewin, D. J. Adams, A. I. Cooper, Chem. Sci. 2011, 2, 1777.
- 32 S. N. Habisreutinger, L. Schmidt-Mende, J. K. Stolarczyk, Angew. Chem. Int. Ed. 2013, **52**, 7372.
- 33 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Y. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, J. A., J. E. Peralta, F. Ogliaro, M. Bearpark, E. B. Heyd, J. J., K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision A.02 2009.
- 34 T. W. Woolerton, S. Sheard, E. Reisner, E. Pierce, S. W. Ragsdale, F. A. Armstrong, *J. Am. Chem. Soc.* 2010, **132**, 2132.

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Task-specific ionic liquid in combination with a pyrene-based conjugated polymer realizes the direct capture of CO_2 and H_2O from air and further conversion to CO under visible-light irradiation.