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Assembling 4f and 3d–4f clusters as single-molecule magnets by automatic fixation of atmospheric CO₂

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Emerging methods for cluster assembly through fixation of CO₂ in air provide an innovative approach for the development of novel single-molecule magnets (SMMs). Both 4f cluster SMMs and 3d–4f cluster SMMs may be assembled using this green pathway. Even after the introduction of chirality and/or inter-molecular hydrogen bonds, such SMMs can be further made into multifunctional molecular materials at the nanoscale. In this paper, 4f cluster SMMs and 3d–4f cluster SMMs assembled by the fixation of CO₂ in air are briefly reviewed, and an outlook of the promising future prospects in this field is provided.

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1. Introduction

Global warming due to the massive emission of CO₂ has attracted widespread attention. By innovating energy technologies and reducing tailpipe emissions, we can directly reduce the greenhouse effect. On the other hand, some progress has been made in fixing and converting atmospheric CO₂ into organic molecules¹ and CO,² which can “turn waste into treasure” and realize the carbon cycle to reduce the greenhouse effect too. However, further costs need to be decreased. In the field of coordination chemistry, chemists may imitate the permanent carbon fixation method of “mineral carbonization”,³ so that the CO₂ in air directly reacts *in situ* with solvents or ligands to form bridging ligands, such as carbonate,^{4–7} mono-methyl anion carbonate,⁸ carbamate,^{9,10} *etc.*, which are then self-assembled into complexes; since the structures of such complexes are even different from those of complexes formed when reactants such as carbonates are directly used,¹¹ a unique green pathway is provided for the construction of new functional complexes, especially for single-molecule magnets (SMMs).

SMMs are molecule-based magnets with magnetic bistability at the nanoscale,¹² and have shown potential applications in the fields of high-density information storage, molecular spintronics and quantum computing. SMMs require both large ground-state spin values and obvious magnetic anisotropies. Lanthanide(III) ions, such as the Dy(III) ion, naturally

meet these two necessary conditions, and are generally used to construct SMMs, including 4f SMMs¹³ and 3d–4f SMMs.¹⁴ It is important to note that for the cluster complexes containing multiple Ln(III) ions it is often hard to exhibit good SMM performance due to the difficulty in maintaining consistent magnetic axis orientation across all Ln(III) ions.^{15,16} Therefore, it is particularly important to select an appropriate bridging ligand to link cations such as the Ln(III) ions. The carbonate anion, the most common product of CO₂ fixation, is exactly a suitable ligand that may bridge three or more Ln(III) ions.¹⁷ It can also transfer ferromagnetic interactions, which is beneficial to obtain zero-field SMMs.¹⁸ In addition, it is an excellent functional structural unit of nonlinear optical double-frequency effects,¹⁹ and is thus suitable for the construction of multifunctional molecular materials. What's more, under suitable conditions, the *in situ* reaction process of immobilizing CO₂ to form the carbonate or other bridging ligands can be perfectly matched to the self-assembly process of 4f and 3d–4f SMMs, whose single crystals can be directly grown and easily separated. Therefore, the fixation of atmospheric CO₂ provides a unique green approach for the development of novel SMMs. Herein related zero-field SMMs and multifunctional SMMs are focused.

2. Fixation of atmospheric CO₂ for the assembly of 4f cluster SMMs

Since CO₂ is a weakly acidic gas, an alkaline solution helps in its automatic capture and fixation.²⁰ The commonly used alkaline reagents include NaOH, NaOMe, LiOH, KOH, KOBu^t, Et₃N, Me₄NOH·5H₂O, pyridine and so on. In some cases, organic amines with hydroxyl groups such as triethanol-

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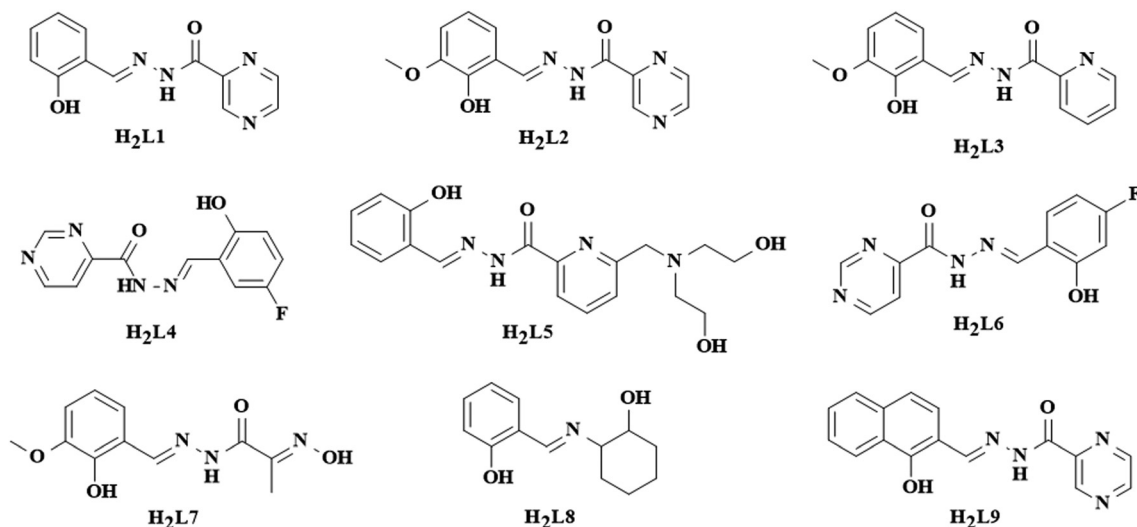
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amine²¹ are even used as alkaline reagents. There is no doubt that suitable organic ligands play a critical role in assembling 4f cluster SMMs by the fixation of atmospheric CO₂. Schiff bases, especially those formed by the condensation of hydrazide and salicylaldehyde (or salicylaldehyde with substituents) (Scheme 1), show unique advantages in this area. H₂L1 in Scheme 1 was reacted with DyCl₃·6H₂O and Et₃N in MeOH-CH₂Cl₂, which resulted in the formation of a Dy₆ SMM based on vertex- and edge-sharing Dy₃ triangles, [Dy₆(μ³-OH)₃(μ³-CO₃)(μ-OMe)(HL1)₆(MeOH)₄(H₂O)₂]·3MeOH·2H₂O (1), which contains an unusual η²:η²-μ₃-CO₃²⁻ carbonate bridging ligand sourced from the atmospheric CO₂ and shows two clear relaxation regimes, with *U/k* values of 5.6 K and 37.9 K at 0 Oe;²² this ligand could also be reacted with Dy(OAc)₃·6H₂O and Et₃N in MeOH-CH₂Cl₂, yielding another Dy₆ SMM, [Dy₆(μ⁴-CO₃)₃(μ³-H₂O)(L1)₆(MeOH)₆(H₂O)₃]·4MeOH·3H₂O (2), in which three CO₃²⁻ groups derived from the fixation of CO₂ in air are located on the sides of the triangular prism of Dy₆;²³ complex 2 also displays double magnetic relaxation, with *U/k* values of 5.4 K and 186.8 K at 0 Oe.²³ In H₂L2 (Scheme 1), there is an additional methoxy group compared to H₂L1. When H₂L2 was reacted with Dy(OAc)₃·6H₂O and Et₃N in MeOH-EtOH-CH₂Cl₂, a trigonal prism Dy₆ cluster, [Dy₆(OAc)₃(μ₃-CO₃)₂(L2)₅(HL2)(MeOH)₂]·4H₂O·5MeOH·EtOH (3), could be produced by the fixation of CO₂ in air,²⁴ in which two CO₃²⁻ anions are located on the two bases of the triangular prism and three AcO⁻ anions are involved in coordination; complex 3 is a zero-field SMM, with an *U/k* value of 56 K.²⁴ Interestingly, when Dy(OAc)₃·6H₂O was replaced with DyCl₃·6H₂O and MeOH-EtOH-CH₂Cl₂ with MeOH-CH₂Cl₂, a quadruple-CO₃²⁻ bridged Dy₈ cluster, [Dy₈(μ₄-CO₃)₄(L2)₈(H₂O)₈]·10MeOH·2H₂O (4), could be yielded by fixating atmospheric CO₂ too, where four CO₃²⁻ anions are located on the four lateral faces of the square prism Dy₈;²⁵ complex 4 shows intramolecular ferromagnetic interactions and is a zero-field SMM with an *U/k* value of 74.2 K; in addition, it has an obvious hysteresis loop at 1.9 K.²⁵

Furthermore, when H₂L3 (Scheme 1), a Schiff base ligand similar to H₂L2 but with a pyridine ring instead of a pyrazine ring, was reacted with DyCl₃·6H₂O and Et₃N in MeOH-MeCN, another double-CO₃²⁻ bridged trigonal prism Dy₆ cluster, [Dy₆(L3)₄(HL3)₂Cl₄(H₂O)₂(CO₃)₂]·CH₃OH·H₂O·MeCN (5), might be obtained,¹¹ in which four Cl⁻ anions are involved in coordination; complex 5 is also a zero-field SMM with an *U/k* value of 76 K.¹¹ Thus, the anions can alter the structures and compositions of 4f cluster SMMs assembled by the fixation of atmospheric CO₂.

The choice of anions also determines whether the reaction of Dy(III) cluster SMMs assembled by the immobilization of atmospheric CO₂ can be carried out. H₂L4 (Scheme 1) was reacted with different dysprosium(III) salts in an alkaline solution to assemble Dy(III) clusters with different nuclei, depending on whether the anion used is NO₃⁻ or Cl⁻. The double-CO₃²⁻ bridged trigonal prism Dy₆ cluster [Dy₆(CO₃)₂(L4)₆(H₂O)₃(MeOH)Cl]₂·5MeOH (6) was formed by fixing CO₂ in air, in which two Cl⁻ anions participate in coordination, and complex 6 is a zero-field SMM, with an *U/k* value of 150.9 K;²⁶ however, when the reaction was carried out with Dy(NO₃)₃·5H₂O, a Dy₄ cluster SMM was obtained, which does not involve the fixation of CO₂ in air.²⁶ A similar trend was observed when H₂L5 (Scheme 1) was used to construct Dy(III) SMMs: when DyCl₃·6H₂O was used, a propeller-shaped Dy₆ cluster, [Dy₆(H₂L5)₃(μ₃-OH)(μ₃-CO₃)₃(CH₃OH)₄(H₂O)₈]·5Cl·3H₂O (7), was obtained, in which each CO₃²⁻ group derived from the CO₂ fixation is linked to two Dy³⁺ ions from both the small triangular Dy₃ and the large triangular Dy₃, and complex 7 is a SMM at 0 Oe, showing double relaxation of magnetization, with *U/k* values of 2 K and 62.4 K;²⁷ however, when Dy(NO₃)₃·5H₂O was used, a Dy₂ SMM without the CO₂ fixation was yielded.²⁷

The reaction solvent also has an effect on the construction of Dy(III) SMMs assembled by the fixation of atmospheric CO₂. When H₂L6 (Scheme 1) was used to construct Dy(III) cluster SMMs containing the CO₂ immobilized bridging ligands, it was



Scheme 1 Some Schiff base ligands for the assembly of 4f cluster SMMs by the automatic fixation of atmospheric CO₂.

surprising that the small differences between the MeOH and EtOH solvents led to a dramatic change in the structures of the Dy(III) cluster complexes (Fig. 1).²⁸ When MeOH participated in the reaction, a trapezoidal pyramidal Dy₅ pentanuclear cluster, [Dy₅(L6)₅(OH)₂(CO₃)(O₂COME)(MeOH)₃(H₂O)]·3MeOH·3.5H₂O (**8**), was obtained,²⁸ in which both the carbonate anion and the monomethyl carbonate anion are formed by the atmospheric CO₂ fixation, and complex **8** is a zero-field SMM, with an *U/k* value of 93.2 K;²⁸ however, when EtOH participated in the reaction, a triangular prism Dy₆ cluster, [Dy₆(L6)₆(CO₃)₂(EtOH)₂(H₂O)₂Cl₂]·6EtOH (**9**), was obtained,²⁸ in which only the carbonate anion exists, and complex **9** is also a zero-field SMM, with an *U/k* value of 133.5 K.²⁸ Notably, **8** and **9** can form hysteresis loops at 1.9 K and 2.0 K, respectively.²⁸ Moreover, the coordination solvents also have an effect on the magnetic properties of 4f cluster SMMs involved in the CO₂ immobilization. In different mixed solvents, two parallelogram Dy₄ SMMs could be obtained by fixing CO₂ in air using H₂L7 (Scheme 1), [Dy₄(CO₃)(L7)₄(acac)₂(H₂O)₄]·2CH₃CN (**10**) and [Dy₄(CO₃)(L7)₄(acac)₂(CH₃OH)₂(H₂O)₂]·CH₃OH·H₂O (**11**),²⁹ where two MeOH molecules in **11** are coordinated instead of two H₂O molecules in **10**, and consequently, the *U/k* value increases obviously from 2.7 K at 0 Oe in **10** to 23.8 K at 0 Oe in **11**.²⁹

The Schiff bases derived from organic amines with hydroxyl groups can also be used to assemble Ln(III) cluster SMMs with the fixation of atmospheric CO₂. For example, H₂L8 (Scheme 1) was treated with Dy(ClO₄)₃·6H₂O and Me₄NOH·5H₂O in MeOH to produce a metal-centred trigonal prismatic Dy₇ cluster, [Dy₇(OH)₆(CO₃)₃(L8)₃(HL8)₃(MeOH)₆] (**12**),³⁰ in which three CO₃²⁻ anions derived from the CO₂ fixation are located on the sides of the triangular prism; complex **12** displays weak SMM properties, with a small *U/k* value of ~1.7 K.³⁰

Interestingly, homochiral Ln(III) cluster SMMs formed by the fixation of atmospheric CO₂ can also be constructed with the Schiff base ligand. For example, H₂L9 (Scheme 1) and L/D-proline were used to construct a pair of homochiral triangular Dy₆ cluster complexes, [Dy₆(CO₃)(L/D-Pro)₆(L₉)₄(HL₉)₂]·5DMA·2H₂O (L-**13** and D-**13**),³¹ which contain a centre CO₃²⁻ bridging ligand

that originated from the fixation of atmospheric CO₂. Although only small *U/k* values of ~6.5–8.3 K are observed for L-**13**/D-**13**, they have clear magneto-optical Faraday effects and show a large SHG response (1.0× KDP).³¹ Therefore, the immobilization of atmospheric CO₂ can be used to assemble homochiral multi-functional 4f cluster complexes.

3. Fixation of atmospheric CO₂ for the assembly of 3d–4f cluster SMMs

Schiff bases and their hydrogenated derivatives or analogues also play a leading role in the assembly of 3d–4f SMMs by the immobilization of atmospheric CO₂ in alkaline media.^{32–41} H₂L10 (Scheme 2) and tetramethylheptanedione (Hthd) were used to assemble a Cu–Tb heterometallic SMM, Cu(L10)(O₂COME)Tb(thd)₂ (**14**),³³ in which the monomethyl carbonate ligand was formed by the fixation of atmospheric CO₂ in MeOH in the presence of LiOH·H₂O, and complex **14** is a zero-field SMM, with an *U/k* value of 13.8 K.³³

The coordination solvents also have an effect on the magnetic properties of 3f–4f SMMs produced by atmospheric CO₂ fixation.^{34,35} In MeOH–Me₂CO, H₂L11 (Scheme 2) was used to construct Ni₂Ln₂ complexes [(μ₄-CO₃)₂{Ni(L11)(MeOH)Tb(NO₃)₂}₂] (**15**) and [(μ₄-CO₃)₂{Ni(L11)(MeOH)Dy(NO₃)₂}₂] (**16**);³⁵ however, in MeCN–H₂O, other two Ni₂Ln₂ complexes [(μ₄-CO₃)₂{Ni(L11)(H₂O)Tb(NO₃)₂}₂] (**17**) and [(μ₄-CO₃)₂{Ni(L11)(H₂O)Dy(NO₃)₂}₂] (**18**) were formed,³⁵ in which the coordinated H₂O molecules take the place of the coordinated MeOH molecules in **15** and **16**. Two Ni(II)–Ln(III) units in **15**–**18** are bridged by two carbonate ligands from the atmospheric CO₂ fixation. The *U/k* value of **15** (12.2 K at 1000 Oe) is larger than that of **17** (6.1 K at 1000 Oe),³⁵ similarly, the *U/k* value of **16** (18.1 K at 1000 Oe) is larger than that of **18** (14.5 K at 1000 Oe), and **16** even can show SMM behaviour at 0 Oe, with an *U/k* value of 6.6 K.³⁵ These results indicate that the coordinated MeOH molecule is better for this type of SMM performance than the coordinated H₂O molecule.

The salen ligand H₂L11 (Scheme 2) was also used to assemble Zn₂Ln₂ SMMs by the immobilization of CO₂ in air. Two Zn₂Ln₂ cluster complexes Zn₂Dy₂(μ³-CO₃)₂(L11)₂(NO₃)₂(MeOH)₂ (**19**) and Zn₂Tb₂(μ³-CO₃)₂(L11)₂(NO₃)₂(MeOH)₂ (**20**) were synthesized using this ligand;³⁶ similarly, another salen ligand H₂L12 (Scheme 2) was used to construct two other Zn₂Ln₂ cluster complexes, [Zn₂Dy₂(μ³-CO₃)₂(L12)₂(NO₃)₂]·2MeOH (**21**) and [Zn₂Tb₂(μ³-CO₃)₂(L12)₂(NO₃)₂]·2MeOH (**22**);³⁶ **19** shows double magnetic relaxation at 1500 Oe, with *U/k* values of 18.8 K and 41.0 K, while **20** shows double magnetic relaxation at 1200 Oe, with *U/k* values of 12.4 K and 31.4 K; **21** exhibits SMM behaviour at 2000 Oe, with an *U/k* value of 54.0 K, while **22** shows SMM behaviour at 1200 Oe, with an *U/k* value of 26.9 K; interestingly, **21** and **22** display characteristic fluorescence of the Tb(III) ions, and the lifetime (τ) of **21** (20.6 μs) is longer than that of **22** (4.6 μs).³⁶ These results indicate that the structures, magnetic and luminescence properties of these Zn–Ln cluster SMMs may be adjusted by the bisimine chain of the Schiff base ligands.

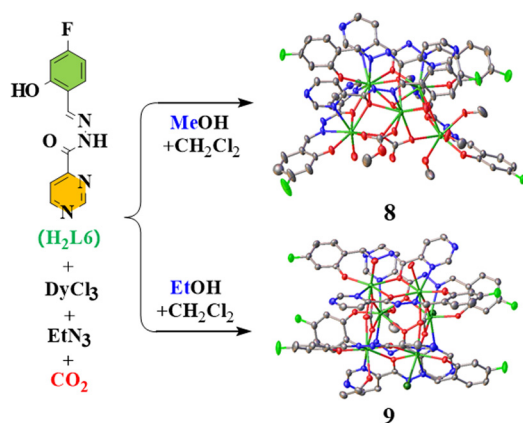
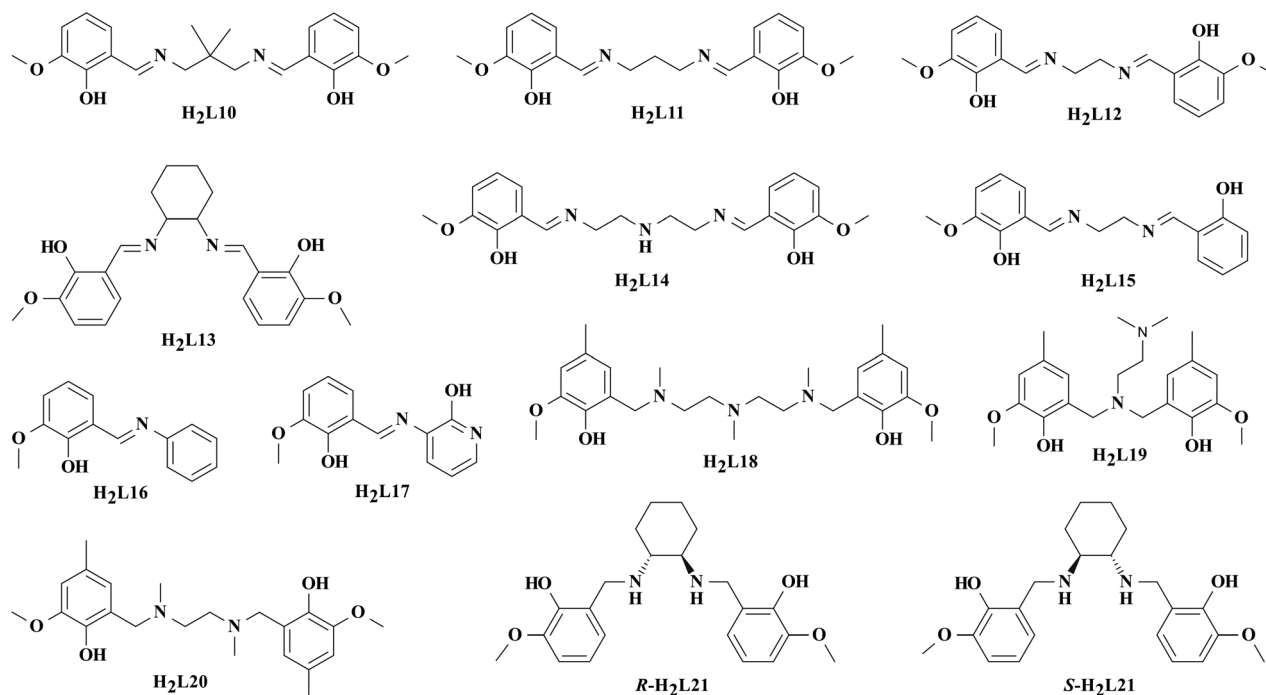


Fig. 1 MeOH and EtOH solvents have a dramatic effect on the construction of Dy(III) cluster SMMs (**8** and **9**) assembled by the fixation of atmospheric CO₂.



Scheme 2 Some ligands for the assembly of 3d–4f cluster SMMs by the automatic fixation of atmospheric CO₂.

Another salen ligand, H₂L13 (Scheme 2), was used to synthesize a similar Zn₂Dy₂ SMM containing the CO₃^{2−} bridging ligand from CO₂, [Dy₂Zn₂(L13)₂(OAc)₂(CO₃)₂]₂·10CH₃OH (**23**); it is a zero-field SMM, with an *U/k* value of 34 K.³⁷ Surprisingly, when H₂L14 (Scheme 2) was adopted to prepare 3f–4f SMMs by the fixation of atmospheric CO₂, a carbamate ligand (L_{carbamate}) was formed automatically through an *in situ* ligand reaction of H₂L14, and both [Zn₄Dy₂(L14)₂(L_{carbamate})₂(N₃)₂]Cl₂·2H₂O (**24**) and [Zn₄Tb₂(L14)₂(L_{carbamate})₂(Cl)₂][ZnN₃Cl₃]·2H₂O (**25**) show SMM behaviours under a dc field, with *U/k* values of 30.67 K at 1000 Oe for **24** and 8.9 K at 2000 Oe for **25**.¹⁰

Asymmetric Schiff bases have also been used in the synthesis of 3d–4f cluster SMMs involving CO₂ fixation.^{38–40} The Ni²⁺ complex precursor derived from H₂L15 (Scheme 2), NiL15, was pre-synthesized; it was then reacted with DyCl₃·6H₂O in MeOH–MeCN to obtain a Ni₄Dy₂ cluster, [Ni₄Dy₂(CO₃)₂Cl₂(L15)₂(L')₂(MeCN)₂]·4MeCN·2H₂O (H₂L' = *N,N'*-bis(salicylidene)-1,3propanediamine) (**26**),³⁸ which contains the carbonate bridging ligand from the CO₂ immobilization and shows SMM behaviour at 2000 Oe, with an *U/k* value of ~40 K.³⁸ When H₂L16 (Scheme 2) was treated with Dy(NO₃)₃·5H₂O, Ni(NO₃)₃·6H₂O and Et₃N in MeOH, another Ni₂Dy₂ cluster, [Ni₂Dy₂(L16)₂(*o*-vanillin)₂(CO₃)₂(NO₃)₂(MeOH)₂] (**27**), was yielded, which exhibits possibility of SMM behaviour.³⁹ Notably, the co-ligand may play an important role in the assembly of such 3d–4f cluster SMMs; for example, when di-2-pyridyl ketone (dpk) was treated with H₂L16 (Scheme 2), Ni(NO₃)₃·6H₂O, Dy(NO₃)₃·5H₂O and Et₃N, a Ni₄Dy₄ cluster, [Ni₄Dy₄(L17)₆(L')₂(py)₂C(OCH₃)O)₂(μ³-CO₃)₂(CH₃OH)₂]·10CH₃OH·13H₂O (**28**), was obtained,⁴⁰ in which the new ligand (py)₂C(OCH₃)O was generated by an *in situ*

ligand reaction of dpk, and the latter also provides an alkaline reaction environment for the immobilization of CO₂; complex **28** is a zero-field SMM, with an *U/k* value of 14.9 K.⁴⁰

Schiff base analogues have also been successfully used to assemble several Zn₂Ln₂ SMMs involving atmospheric CO₂ fixation.^{41–43} Two such luminescent Zn₂Ln₂ SMMs, {(μ³-CO₃)₂[Zn(μ-L18)Dy(NO₃)₂]₂·4CH₃OH (**29**)⁴¹ and {(μ³-CO₃)₂[Zn(μ-L18)Yb(H₂O)]₂}(NO₃)₂·4CH₃OH (**30**),⁴² were obtained using H₂L18 (Scheme 2): both **29** and **30** are field-induced SMMs,^{41,42} and the *U/k* value of **29** (24 K at 1000 Oe) is larger than that of **30** (19.4 K at 1000 Oe); however, **29** shows yellow luminescence of the Dy³⁺ ion,⁴¹ while **30** displays near-infrared Dy³⁺-based luminescence.⁴² A Zn₃Dy₃ triangular cluster containing a central μ₆-CO₃^{2−} bridging ligand from the fixation of CO₂ in air, [Zn₃Dy₃(μ₆-CO₃)(μ₃-OH)₃(L19)₃(H₂O)₃]·3ClO₄·NO₃ (**31**), was obtained using H₂L19 (Scheme 2), whose SMM behaviors were studied at 0 Oe and 1000 Oe, with an *U/k* value of 48 K at 1000 Oe.⁴³ Moreover, H₂L20 (Scheme 2) was chosen to prepare another Zn₂Dy₂ SMM with the CO₃^{2−} anion derived from the CO₂ fixation, {Zn₂Dy₂(μ³-CO₃)₂(L20)(acacF₆)₂}-CH₃OH (**32**),⁴⁴ which contains hexafluoroacetylacetone terminal ligands; complex **32** shows magnetic relaxation at 1500 Oe, with an *U/k* value of 83 K.⁴⁴ Importantly, homochiral Schiff base analogues *R*-H₂L21 and *S*-H₂L21 (Scheme 2) were utilized to construct a pair of homochiral Zn₂Ln₂ multifunctional SMMs, [Zn₂Ln₂(*R*-L21)₂(CO₃)₂(NO₃)₂]·2CH₃OH (*R*-**33**) and [Zn₂Ln₂(*S*-L21)₂(CO₃)₂(NO₃)₂]·2CH₃OH (*S*-**33**),¹⁸ which exhibit typical zero-field SMM properties with an *U/k* value of 19.61 K, display the characteristic fluorescence of the Dy(III) ion, and show a weak SHG response (0.051× KDP) (Fig. 2).¹⁸

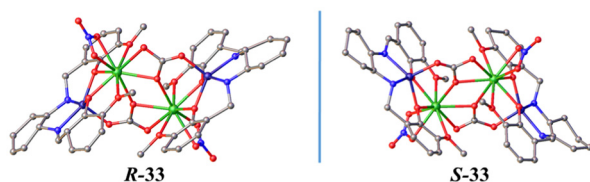


Fig. 2 Mirror-symmetric *R*-33 and *S*-33 assembled by the fixation of atmospheric CO₂.

4. Conclusion and outlook

In this review, 4f cluster SMMs and 3d–4f cluster SMMs assembled by the automatic fixation of atmospheric CO₂ were focused. The high thermodynamic stability of CO₂ and its low concentration in air continue to pose challenges for the synthesis of such SMMs. Many factors, such as basic reagents, anion types, solvents, substituents on ligands, *etc.*, can not only directly affect the occurrence of atmospheric CO₂ fixation, but also affect the structures and properties of 4f cluster SMMs and 3d–4f cluster SMMs after fixing atmospheric CO₂. Notably, in addition to the direct bridging of metal ions as described earlier, the specific structural units of new ligands, which are obtained from the *in situ* reaction of CO₂ in air (such as hydrazine carboxylate⁴⁵), can also be coordinated with metal ions in a non-bridging manner when constructing SMMs, but multi-nuclear (≥ 3) molecular systems are yet to be developed. Furthermore, the introduction of chirality into SMMs can further add new physical properties such as second-order non-linear optics, ferroelectricity, circularly polarized luminescence and magnetochiral dichroism, and the formation of inter-molecular hydrogen bonds has the potential to lead to proton conductivity.⁴⁶ Looking to the future, these molecular engineering and crystal engineering strategies may bring new prospects for the development of nanoscale multifunctional SMMs involving atmospheric CO₂ fixation.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Conflicts of interest

There are no conflicts to declare.

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