



## Supporting Information

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Achieving Dynamic Circularly Polarized Luminescence with 2D Hydrogen-Bonded Organic Frameworks

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Supporting Information for:

## **Achieving Dynamic Circularly Polarized Luminescence with 2D Hydrogen-Bonded Organic Frameworks**

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## General information

Commercially available reagents and organic solvents were used as received without further purification. UV-visible (UV-vis) diffuse reflectance spectra was collected by a U-3900H UV-Vis spectrometer with BaSO<sub>4</sub> as the reference background. Photoluminescence (PL) spectra were measured at room temperature with an F-380 spectrofluorometer. Absolute fluorescence quantum yields ( $\Phi_{\text{FL}}$ ) were measured by a Hamamatsu Absolute PL Quantum Yield Spectrometer C11347 with an integrating sphere. Excited state emission lifetimes were recorded by a Hamamatsu C11367-11 instrument with single photon counting measurement. The morphology of HOF crystals was examined by SEM using Hitachi SU8010 instrument operating at 10 kV. TGA was carried out using the Pyris 1 TGA AIR instrument. N<sub>2</sub> and CO<sub>2</sub> sorption isotherms were performed on Micromeritics ASAP2020HD88 adsorption apparatus. Single-crystal X-ray analysis was performed on the Rigaku Saturn 724 diffractometer on a rotating anode at 173 K with Cu K $\alpha$  radiation (1.54184 Å). The structure was solved by the direct method using SHELXS-97 and refined with Olex2. Powder X-ray diffractions (PXRD) were carried out on the Rigaku D/max-2500 instrument (Cu K $\alpha$ , 1.54 Å). Fluorescence microscopy characterization was carried out using Olympus IX83 Inverted fluorescence microscope equipped with a spot-enhanced charge couple device (CCD, Diagnostic Instrument, Inc.) under UV irradiation (325-375 nm). CD spectra were recorded on a JASCO J-1700 spectrometer. CPL spectra were measured on a JASCO CPL-300 spectrometer.

## Synthesis

Reagents and solvents were used as received. Compound tetra-(4-pyridylphenyl)ethylene (**2**)<sup>1</sup> and 5,5'-bis-(azanediyl)-oxalyldiisophthalic acid (**1**)<sup>2</sup> are known and were synthesized according to the reported literature.

**Preparation of DMF@(**1 2**):** Tetra-(4-pyridylphenyl)ethylene (**2**) (12.8 mg, 0.02 mmol) and 5,5'-bis-(azanediyl)-oxalyldiisophthalic acid (**1**) (21 mg, 0.05 mmol) were added to DMF (2 mL). The reaction mixture was heated in oil bath at 90 °C for 24 h, followed by cooling to room temperature slowly. Green crystals were collected by filtration and washed with cold DMF to give pure DMF@(**1 2**). Yields: 58.3%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  11.26 (s, 2H), 8.72 (d, *J* = 1.5 Hz, 4H), 8.59 (d, *J* = 6.2 Hz, 8H), 8.27 (t, *J* = 1.6 Hz, 2H), 7.95 (s, 0.8H), 7.73 – 7.65 (m, 16H), 7.25 – 7.19 (m, 8H), 2.89 (s, 2.76H), 2.73 (s, 2.66H).

**Preparation of ace@(**1 2**) and (**1 2**):** The freshly prepared DMF@(**1 2**) crystals were immersed in acetone at 50 °C for 96 h. After that, the supernatant was removed, followed by the addition of a proper amount of fresh acetone. This exchange process was repeated for three times to give the crystal of ace@(**1 2**). The obtained crystal of ace@(**1 2**) was further degassed under vacuum at 60 °C for 6 h to afford the solvent-free sample of (**1 2**) as yellow crystals in 79.7% yield. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  11.24 (s, 2H), 8.71 (d, *J* = 1.5 Hz, 4H), 8.66 – 8.53 (m, 8H), 8.27 (t, *J* = 1.6 Hz, 2H), 7.78 – 7.58 (m, 16H), 7.27 – 7.17 (m, 8H). ESI-HRMS (P) calcd for C<sub>64</sub>H<sub>33</sub>N<sub>4</sub> [**2** + H]<sup>+</sup>: 641.2698; found: 641.2670. ESI-HRMS (N) calcd for C<sub>18</sub>H<sub>11</sub>N<sub>2</sub>O<sub>10</sub> [**1** – H]<sup>–</sup>: 415.0417; found: 415.0419.

**Preparation of (+)-car@(**1 2**) and (–)-car@(**1 2**):** The crystals of (+)-car@(**1 2**) and

(-)-car@(**1 2**) were prepared through a similar exchange procedure by immersing ace@(**1 2**) crystals into (+)- or (-)-carvone at 50 °C for 96 h. The obtained cyan crystals were collected by filtration and washed with (+)- or (-)-carvone to give the target samples in 61.4% and 63.5% yield. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 11.24 (s, 2H), 8.71 (s, 4H), 8.59 (d, *J* = 5.3 Hz, 8H), 8.27 (s, 2H), 7.78 – 7.61 (m, 16H), 7.27 – 7.19 (m, 8H), 6.85 (s, 3.18H), 4.76 (d, *J* = 8.7 Hz, 6.78H), 2.68 – 2.62 (m, 3.40H), 2.41 – 2.25 (m, 12.78H), 1.76 – 1.60 (m, 18.94H). ESI-HRMS (P) calcd for C<sub>64</sub>H<sub>33</sub>N<sub>4</sub> [**2** + H]<sup>+</sup>: 641.2697; found: 641.2670. ESI-HRMS (N) calcd for C<sub>18</sub>H<sub>11</sub>N<sub>2</sub>O<sub>10</sub> [**1** – H]<sup>-</sup>: 415.0419; found: 415.0419. ESI-HRMS (P) calcd for C<sub>10</sub>H<sub>14</sub>NaO [carvone + Na]<sup>+</sup>: 173.0937; found: 173.0937.

**Preparation of (+)-cin@(**1 2**) and (-)-cin@(**1 2**):** (+)-cin@(**1 2**) and (-)-cin@(**1 2**) were prepared through a similar exchange procedure by immersing ace@(**1 2**) into (+)- or (-)-cinene at 50 °C for 96 h. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 11.23 (s, 2H), 8.71 (s, 4H), 8.59 (d, *J* = 5.9 Hz, 8H), 8.27 (s, 2H), 7.77 – 7.59 (m, 16H), 7.31 – 7.15 (m, 8H), 5.37 (s, 1.42H), 4.75 – 4.65 (m, 2.85H), 2.10 – 1.89 (m, 6.54H), 1.74 – 1.59 (m, 10.22H), 1.42 – 1.36 (m, 1.79H).

**Table S1.** Crystallographic data and parameters.

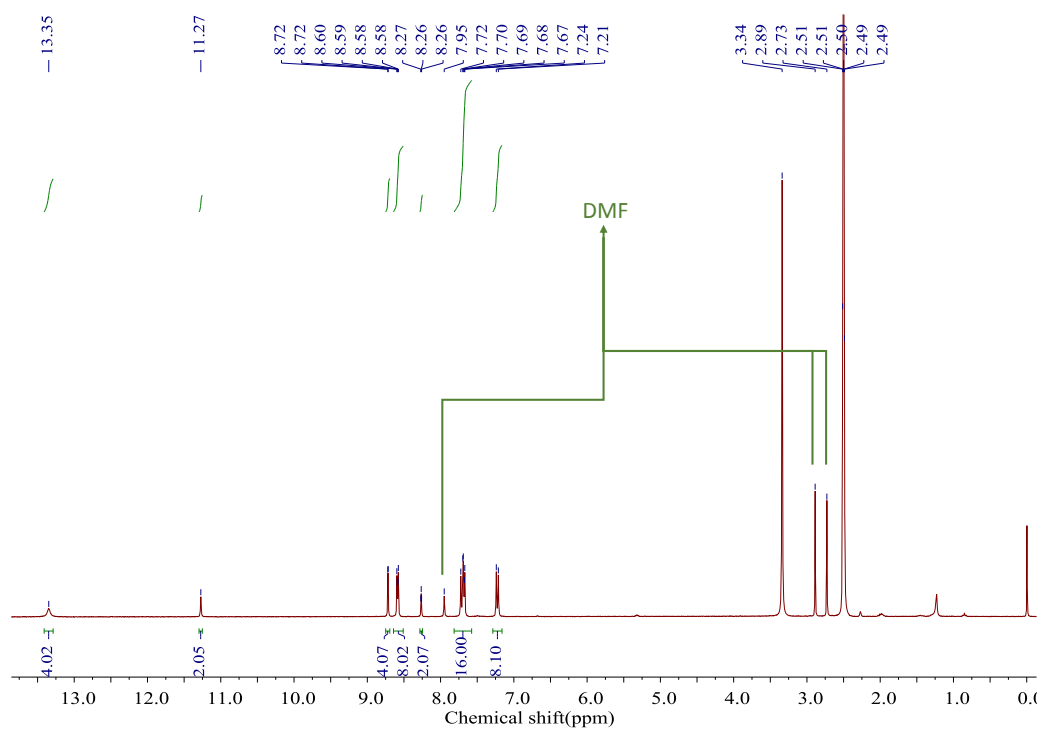
| HOF                          | DMF@( <b>1 2</b> )                                             | ace@( <b>1 2</b> )                                             | (+)-car@( <b>1 2</b> ) <sup>a</sup>                               |
|------------------------------|----------------------------------------------------------------|----------------------------------------------------------------|-------------------------------------------------------------------|
| CCDC number                  | 2305493                                                        | 2305496                                                        | 2400869                                                           |
| empirical formula            | C <sub>70</sub> H <sub>58</sub> N <sub>8</sub> O <sub>12</sub> | C <sub>70</sub> H <sub>56</sub> N <sub>6</sub> O <sub>12</sub> | C <sub>336</sub> H <sub>288</sub> N <sub>24</sub> O <sub>48</sub> |
| formula weight               | 1203.24                                                        | 1173.20                                                        | 5429.89                                                           |
| Temperature (K)              | 170.00(16)                                                     | 170.00(10)                                                     | 169.99(10)                                                        |
| crystal system               | orthorhombic                                                   | orthorhombic                                                   | triclinic                                                         |
| Space group                  | <i>Pbcn</i>                                                    | <i>Pbcn</i>                                                    | <i>P1</i>                                                         |
| a (Å)                        | 36.7823(4)                                                     | 36.8884(8)                                                     | 16.3422(5)                                                        |
| b (Å)                        | 16.0496(3)                                                     | 15.7788(4)                                                     | 24.9025(4)                                                        |
| c (Å)                        | 33.9771(4)                                                     | 33.8166(7)                                                     | 25.2142(3)                                                        |
| $\alpha$ (°)                 | 90                                                             | 90                                                             | 85.1530(10)                                                       |
| $\beta$ (°)                  | 90                                                             | 90                                                             | 85.425(2)                                                         |
| $\gamma$ (°)                 | 90                                                             | 90                                                             | 83.699(2)                                                         |
| V (Å <sup>3</sup> )          | 20058.1(5)                                                     | 19683.1(8)                                                     | 10137.0(4)                                                        |
| Z value                      | 8                                                              | 8                                                              | 1                                                                 |
| Density (g/cm <sup>3</sup> ) | 0.797                                                          | 0.792                                                          | 0.889                                                             |
| R1 (final)                   | 0.0774                                                         | 0.1089                                                         | 0.1049                                                            |
| wR2 (final)                  | 0.2524                                                         | 0.3115                                                         | 0.2841                                                            |
| R1 (all)                     | 0.0956                                                         | 0.1750                                                         | 0.1402                                                            |
| wR2 (all)                    | 0.2717                                                         | 0.3628                                                         | 0.3240                                                            |

<sup>a</sup>The single-crystal quality is relatively low due to the disordered arrangement of the carvone guests, coupled with the issues of twinning and structural disorder. As a result, the crystal exhibits poor diffraction at high angles. See Figure S11.

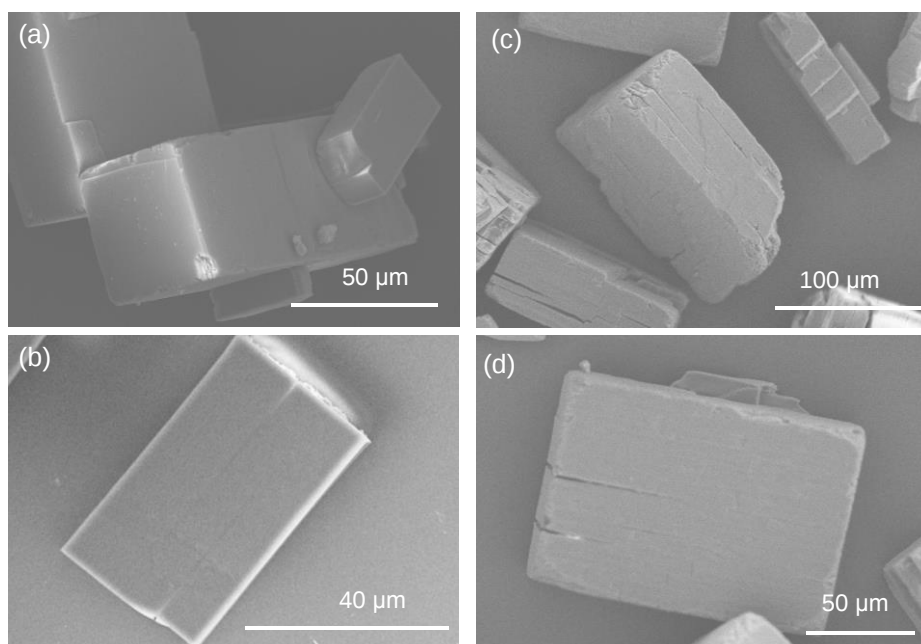
**Table S2.** Photophysics data of microcrystals.

| HOF                                  | $\lambda_{\text{em,max}}/\text{nm}$ | $\tau/\text{ns}$ | $\Phi_{\text{FL}}^{\text{a}}/\%$ | $g_{\text{lum}}^{\text{b}}/(10^{-3})$ |
|--------------------------------------|-------------------------------------|------------------|----------------------------------|---------------------------------------|
| (1 2)                                | 543                                 | 4.65             | 92.5                             | --                                    |
| DMF <sub>2</sub> @(1 2)              | 522                                 | 3.09             | 28.4                             | --                                    |
| ((+)-car) <sub>5.5</sub> @(1 2)      | 495                                 | 2.64             | 28.1                             | -5.10                                 |
| ((-)-car) <sub>4.7</sub> @(1 2)      | 495                                 | 2.62             | 28.2                             | 4.80                                  |
| ((+)-car) <sub>3.2</sub> @(1 2)      | 510                                 | 3.17             | 49.7                             | -5.98                                 |
| ((-)-car) <sub>3.3</sub> @(1 2)      | 510                                 | 2.98             | 47.8                             | 5.09                                  |
| ((+)-car) <sub>1.9</sub> @(1 2)      | 533                                 | 3.65             | 78.8                             | -6.91                                 |
| ((-)-car) <sub>2.5</sub> @(1 2)      | 534                                 | 3.66             | 79.4                             | 6.40                                  |
| ((+)-car) <sub>1.3</sub> @(1 2)      | 540                                 | 2.43             | 54.2                             | -5.27                                 |
| ((-)-car) <sub>1.1</sub> @(1 2)      | 541                                 | 2.79             | 50.8                             | 6.93                                  |
| ((+)-car) <sub>0.3</sub> @(1 2)      | 545                                 | 2.90             | 51.3                             | -4.18                                 |
| ((-)-car) <sub>0.5</sub> @(1 2)      | 545                                 | 2.56             | 51.7                             | 4.60                                  |
| ((+)-car) <sub>&lt;0.01</sub> @(1 2) | 545                                 | 2.76             | 38.9                             | -1.48                                 |
| ((-)-car) <sub>&lt;0.01</sub> @(1 2) | 545                                 | 2.81             | 38.7                             | 1.53                                  |

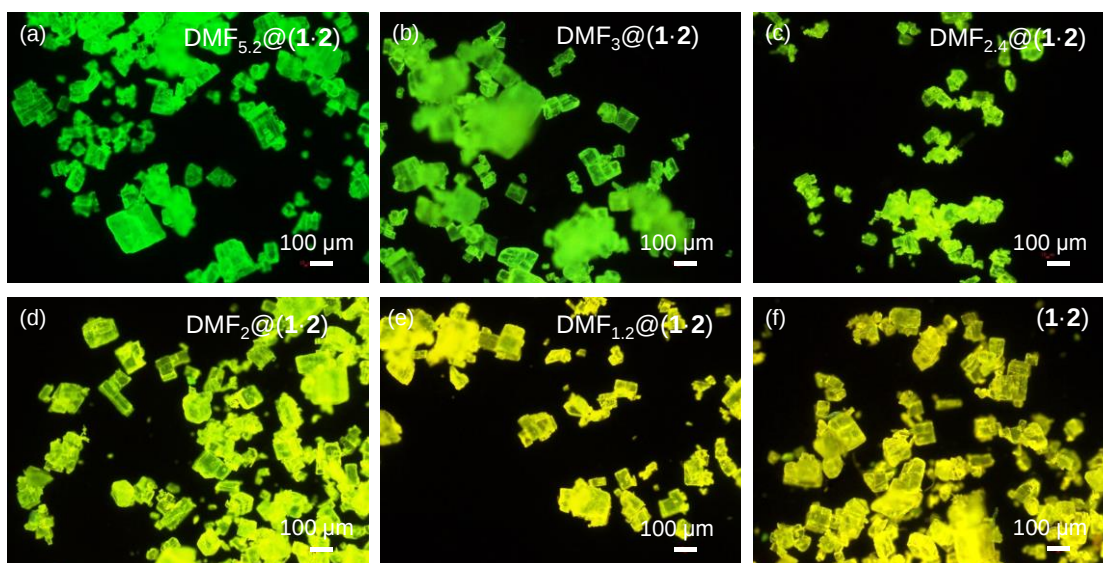
<sup>a</sup>Absolute fluorescence quantum yields. <sup>b</sup>Luminescence dissymmetry is defined as  $2(I_{\text{L}}-I_{\text{R}})/(I_{\text{L}}+I_{\text{R}})$ , where  $I_{\text{L}}$  and  $I_{\text{R}}$  represent the intensity of left- and right-handed CPL, respectively. The values were calculated according to  $g_{\text{lum}} = [\text{ellipticity}/(32980/\ln 10)]/\text{total fluorescence intensity at the CPL extremum}$ .<sup>3</sup> The excitation wavelength is 365 nm for all measurements.



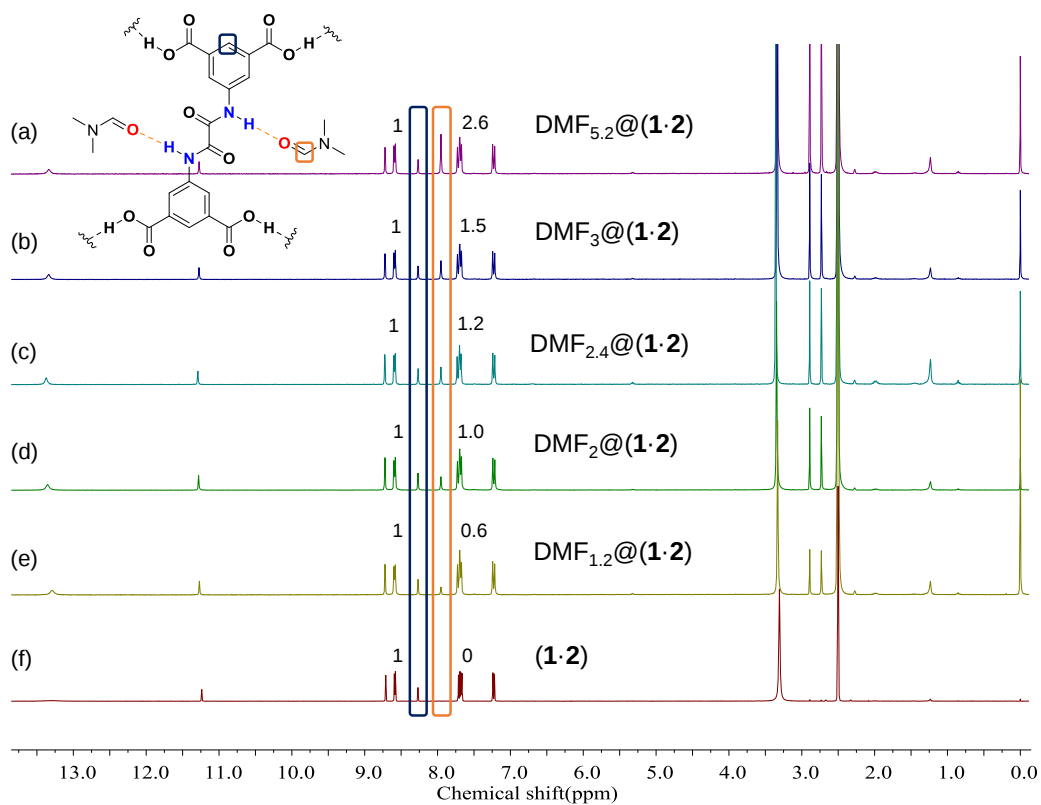
**Figure S1.**  $^1\text{H}$  NMR spectrum of  $\text{DMF}@\text{(1 2)}$  in  $\text{DMSO-}d_6$ .



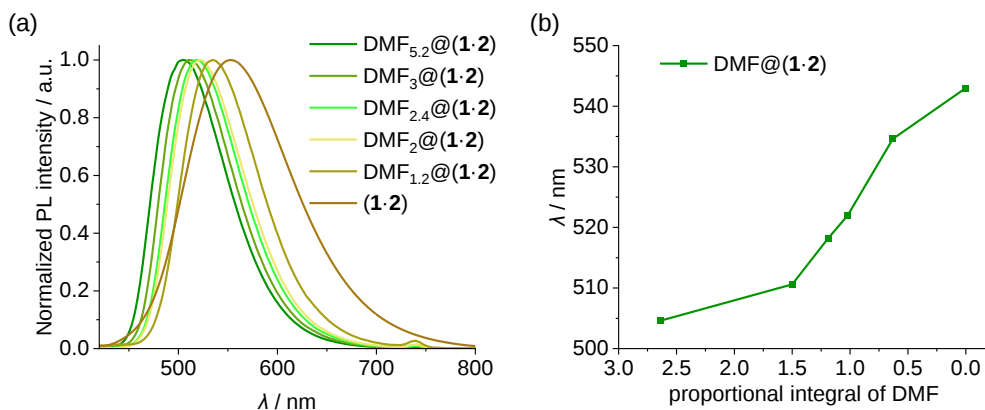
**Figure S2.** SEM images of crystals of (a, b)  $(\text{DMF})_2@\text{(1 2)}$ , (c, d) solvent-free  $\text{(1 2)}$ .



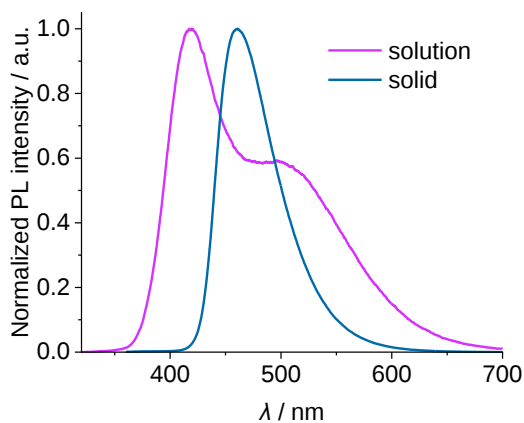
**Figure S3.** Fluorescence microscopy images of DMF@(1·2) containing different contents of DMF.



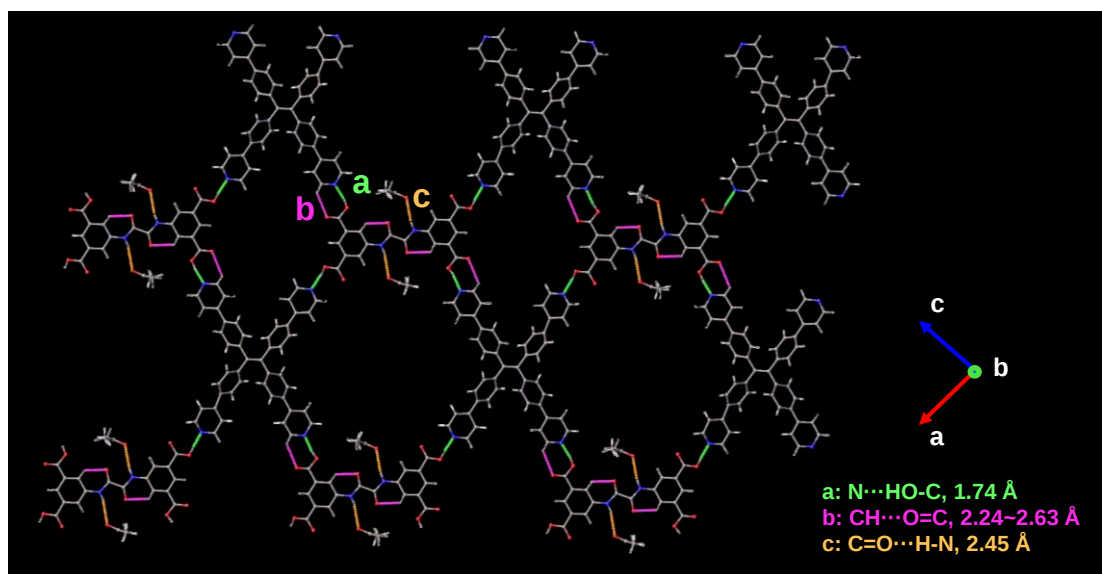
**Figure S4.**  $^1\text{H}$  NMR spectra in  $\text{DMSO-}d_6$  of DMF@(1·2) after storing in air at room temperature for different period. (a) 0 day, (b) 5 days, (c) 15 days, (d) 1 month, (e) 3 months, (f) 6 months. The navy-blue and orange rectangle indicates one phenyl proton of the HOF framework and the DMF aldehyde proton, respectively.



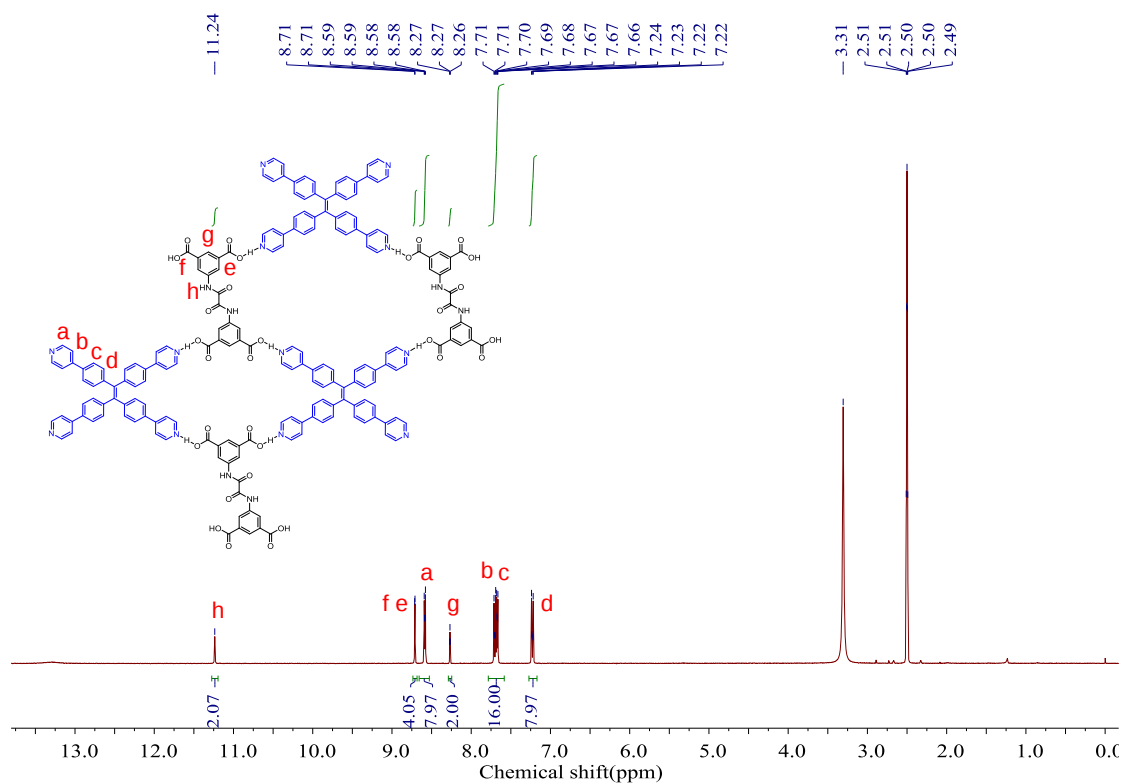
**Figure S5.** (a) Photoluminescence (PL) spectra and (b) plot of proportional integral of DMF vs maximum emission wavelength of DMF@(1·2).



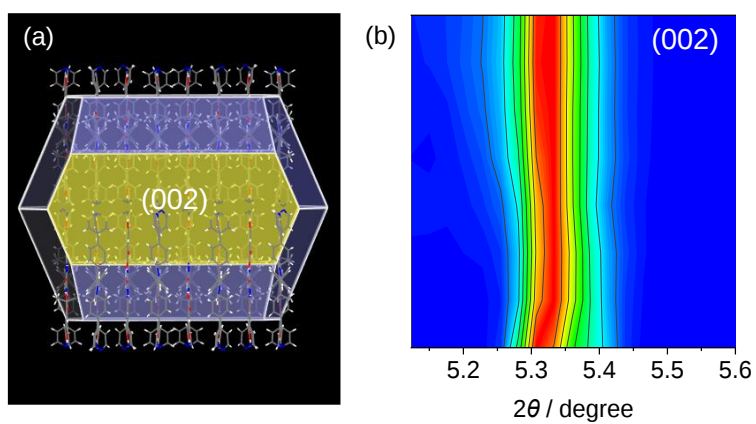
**Figure S6.** PL spectra of **2** in DMF ( $1 \times 10^{-5}$  M) ( $\lambda_{\text{ex}} = 300$  nm) and solid state ( $\lambda_{\text{ex}} = 340$  nm).



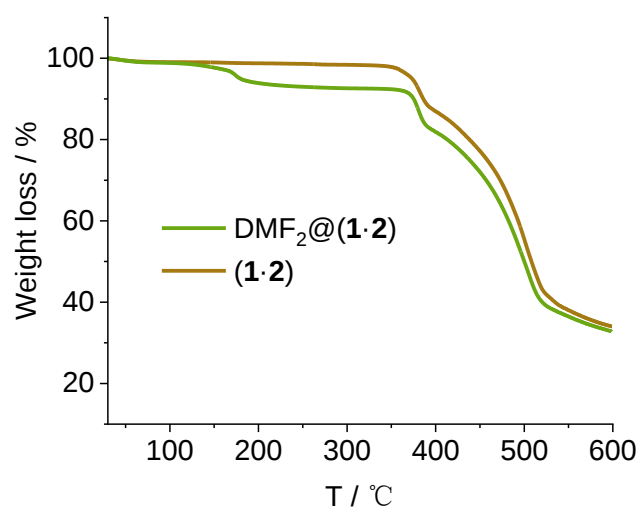
**Figure S7.** Single-layer crystal structure of ace@(1·2) along the crystallographic  $b$  axis, with major non-covalent interactions being indicated.



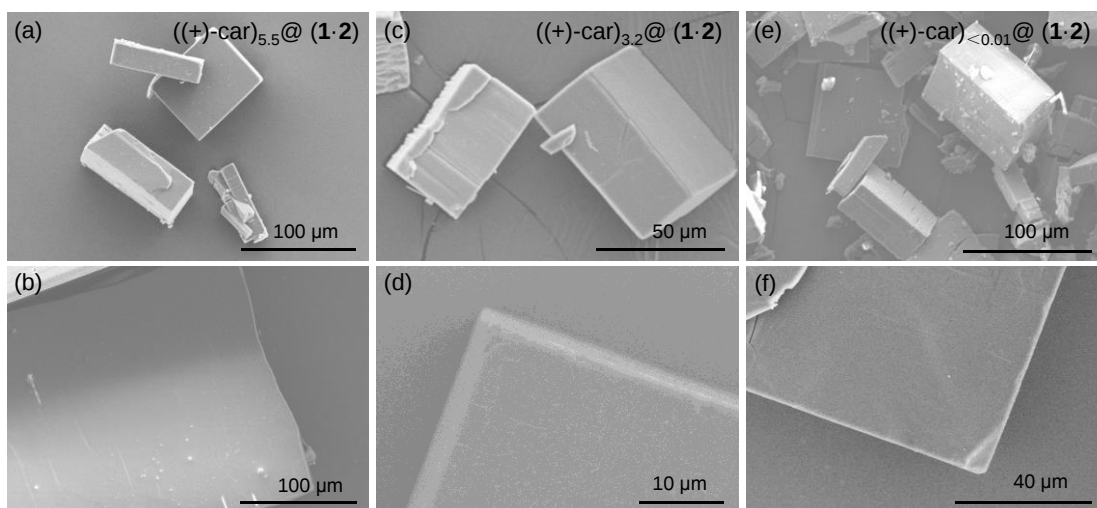
**Figure S8.**  $^1\text{H}$  NMR spectra of (1 2) in  $\text{DMSO}-d_6$ .



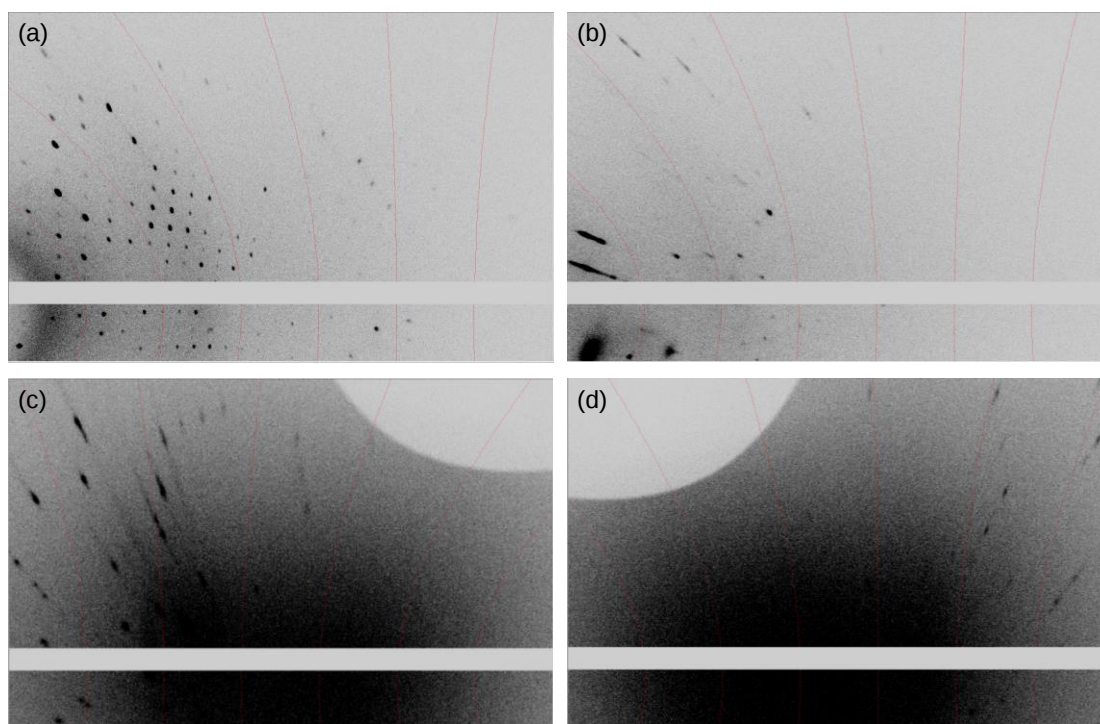
**Figure S9.** (a) Simulated growth morphology of (1 2) viewed from the (002) plane. (b) Evolution of the normalized intensity of the (002) peak of ace@(1 2) upon the desorption of acetone.



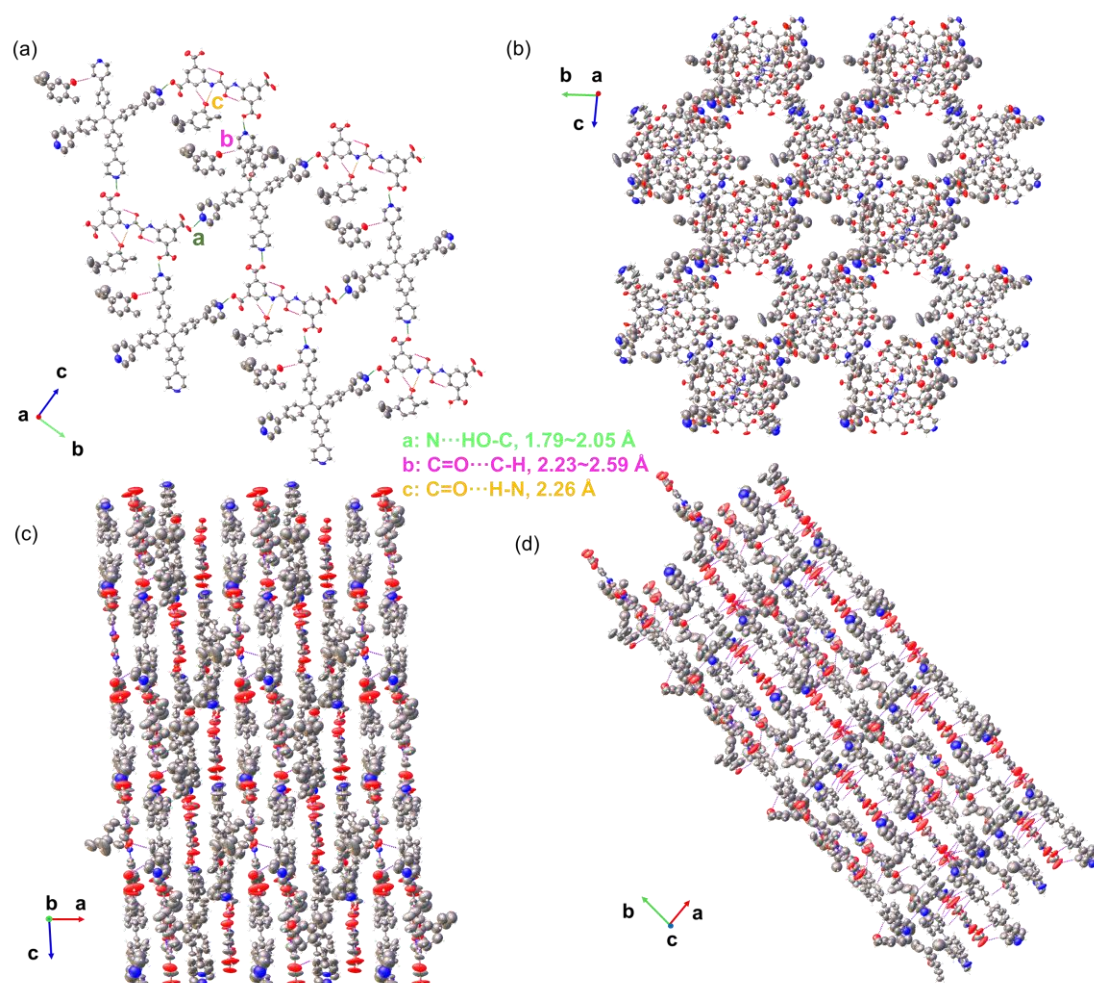
**Figure S10.** TGA curves of DMF<sub>2</sub>@(1.2) and (1.2).



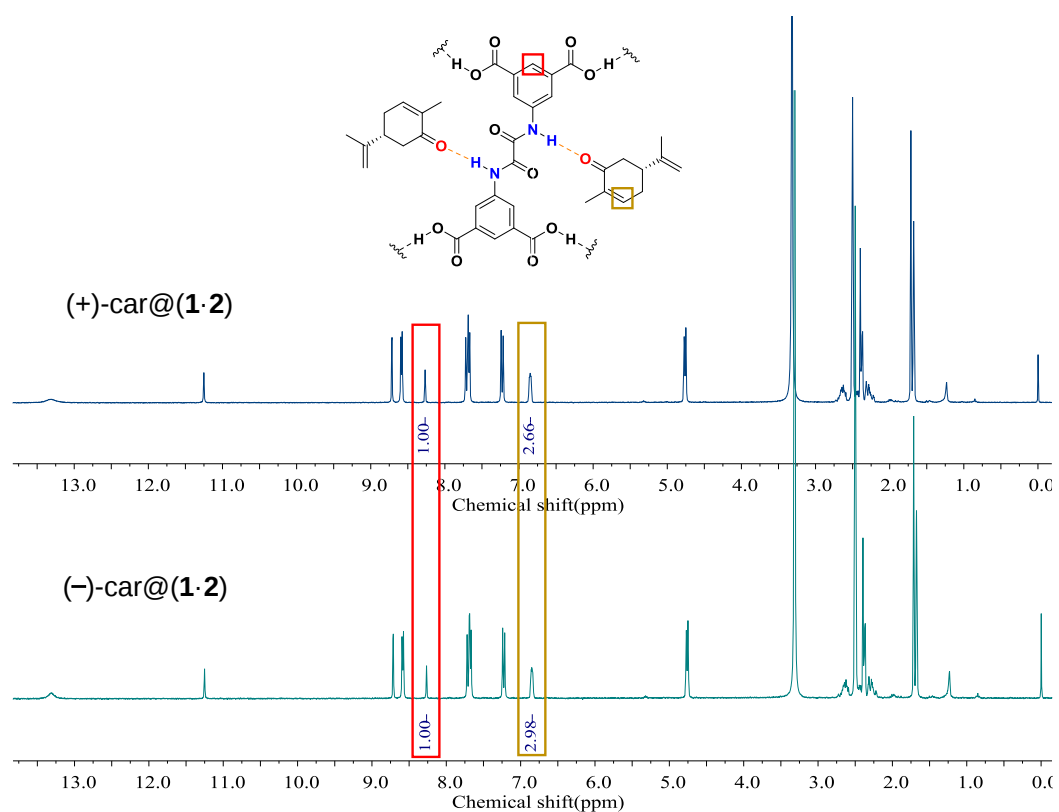
**Figure S11.** SEM images of crystals of (a, b) ((+)-car)<sub>5.5</sub>@(1.2), (c, d) ((+)-car)<sub>3.2</sub>@(1.2) and (e, f) ((+)-car)<sub><0.01</sub>@(1.2).



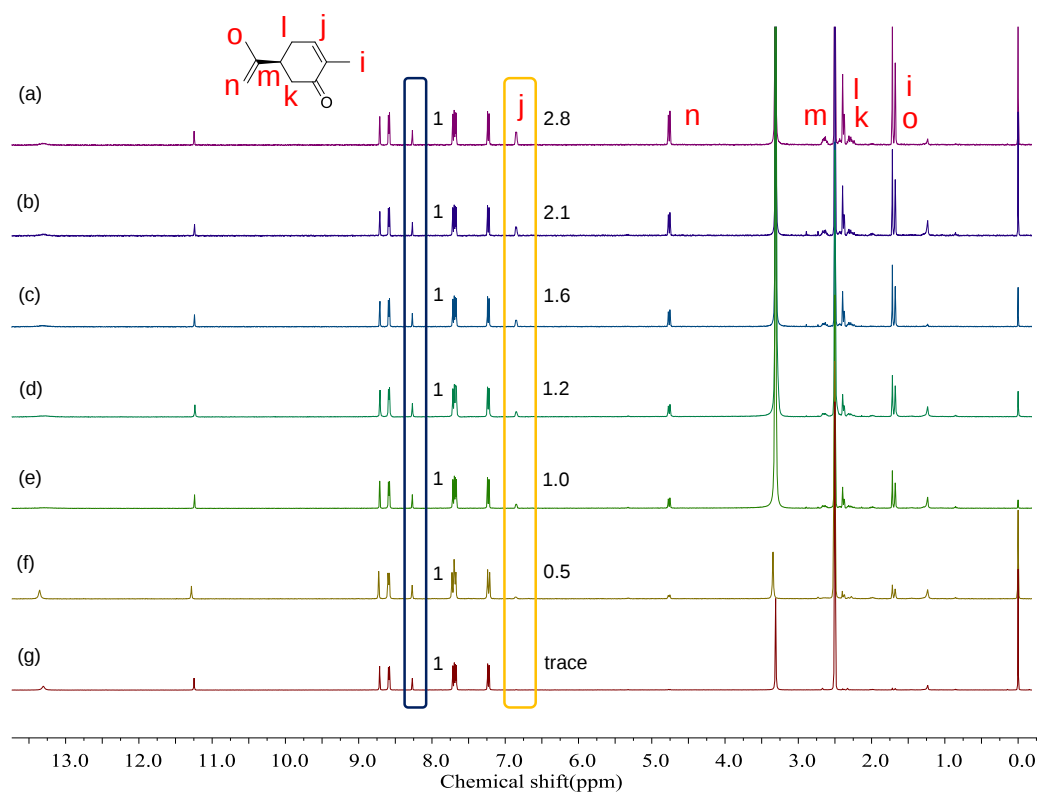
**Figure S12.** Print-screen images of the single frames of the (+)-car@1 2 crystal recorded at (a, b) low diffraction angles and (c, d) high diffraction angles.



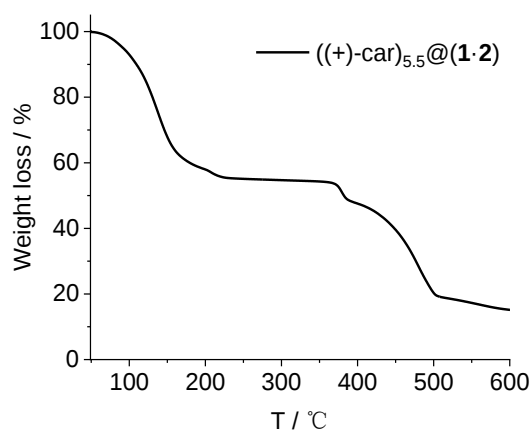
**Figure S13.** (a) Thermal ellipsoid plots at 30% probability of the single-crystal structures of (+)-car@12, with major non-covalent interactions being indicated. (b-d) crystal packing of (+)-car@12 along the crystallographic (b) *a* axis, (c) *b* axis and (d) *c* axis.



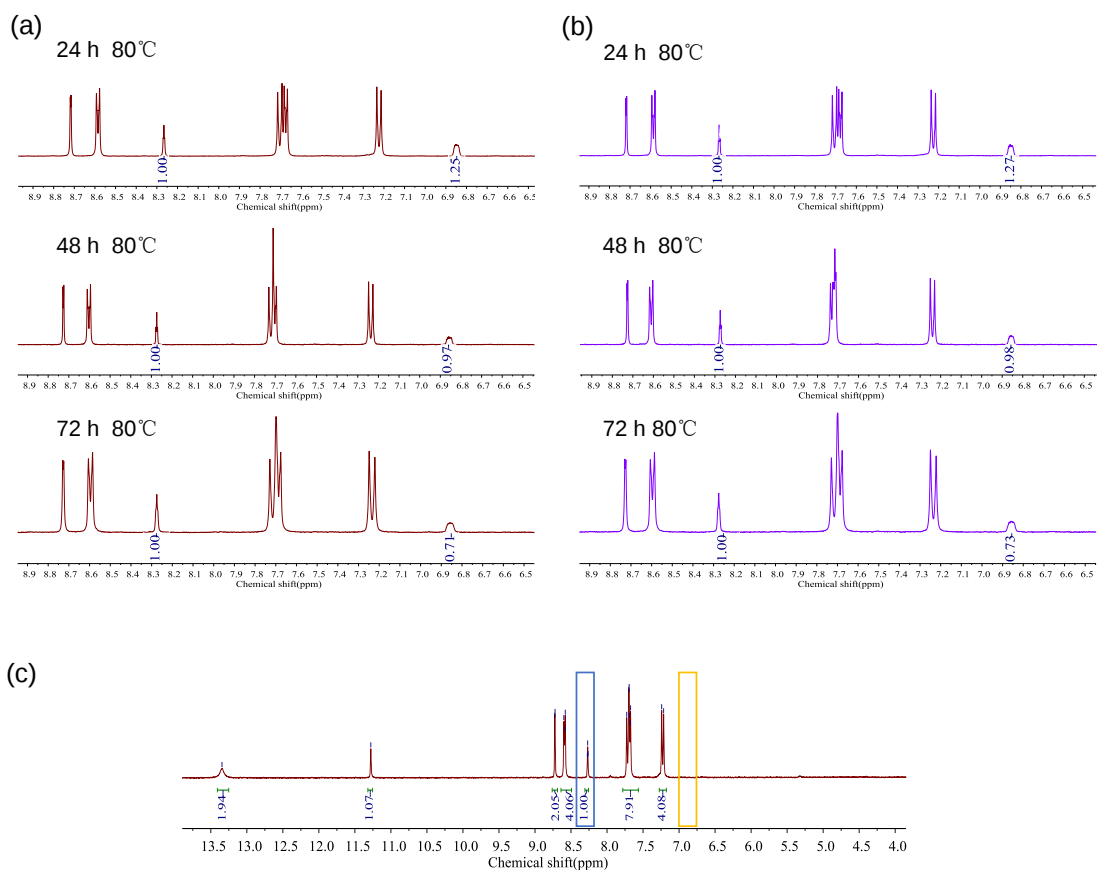
**Figure S14.**  $^1\text{H}$  NMR spectra of freshly prepared (+)-car@(1.2) and (-)-car@(1.2) in  $\text{DMSO}-d_6$ . The red and dark-yellow rectangle indicates one phenyl proton of the HOF framework and one olefin proton of carvone, respectively.



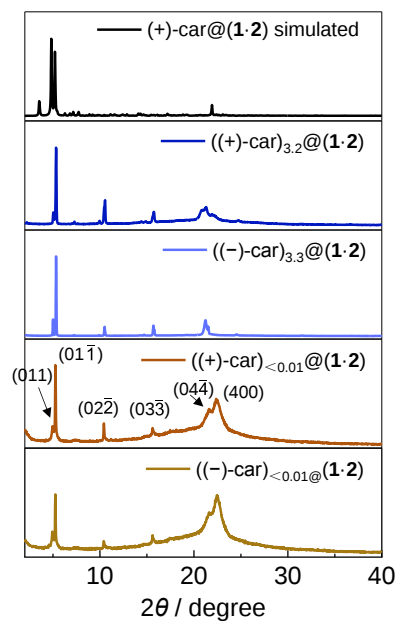
**Figure S15.**  $^1\text{H}$  NMR spectra in  $\text{DMSO-}d_6$  of  $(+)\text{-car@}(1\cdot2)$  after storing in air at room temperature for different period. (a) 0 day, (b) 5 days, (c) 15 days, (d) 1 month, (e) 3 months, (f) 6 months, (g) 12 months. The navy-blue and orange rectangle indicates one phenyl proton of the HOF framework and one olefin proton of carvone, respectively.



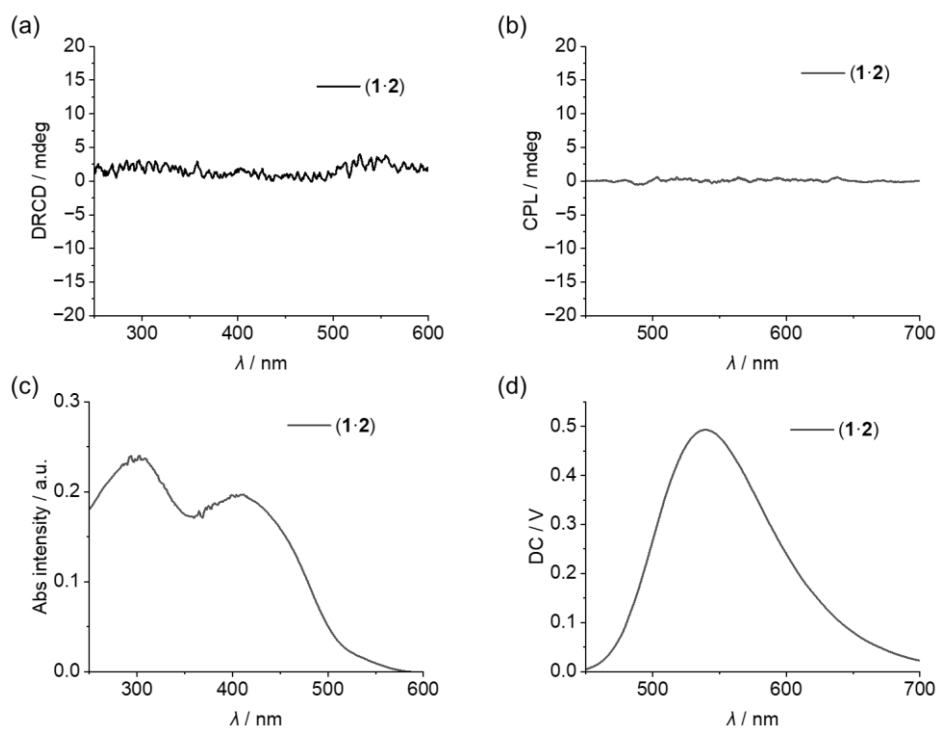
**Figure S16.** TGA curve of  $((+)\text{-car})_{5.5}@1\cdot2$ .



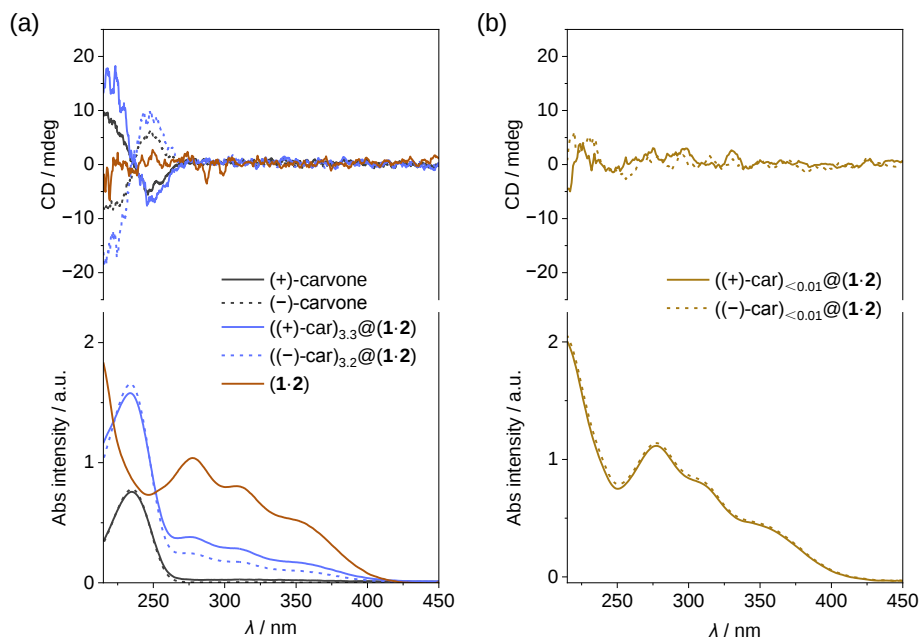
**Figure S17.** (a,b)  $^1\text{H}$  NMR spectra in  $\text{DMSO}-d_6$  of (a) (+)-car@1 2 and (b) (-)-car@1 2 after storing in an open environment at  $80^\circ\text{C}$  for different hours. (c)  $^1\text{H}$  NMR spectrum of ((+)-car) $_{<0.01}$ @1 2 obtained by heating (+)-car@1 2 at  $80^\circ\text{C}$  under vacuum. The navy-blue rectangle indicates one phenyl proton of the HOF framework. The orange rectangle is free of any signal, suggesting that the content of (+)-carvone within this ((+)-car) $_{<0.01}$ @1 2 HOF structure, if any, is negligible.



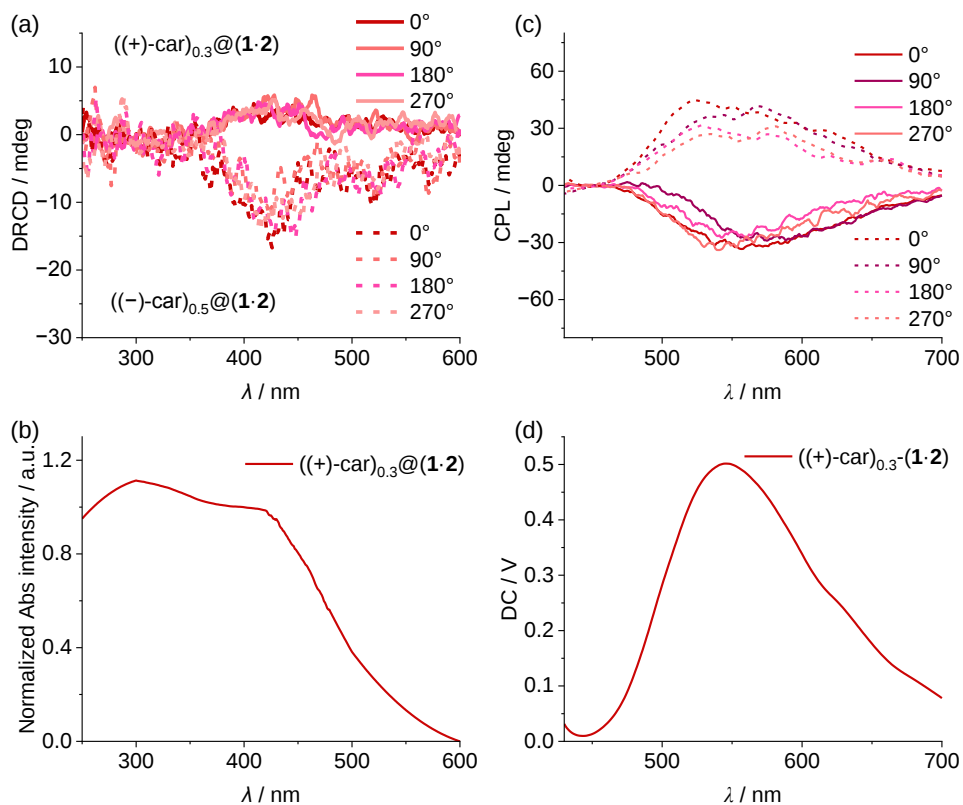
**Figure S18.** PXRD patterns of  $((+)\text{-car})_{3.2}@\text{(1·2)}$ ,  $((-)\text{-car})_{3.3}@\text{(1·2)}$ ,  $((+)\text{-car})_{<0.01}@\text{(1·2)}$  and  $((-)\text{-car})_{<0.01}@\text{(1·2)}$ . The simulated patterns of  $(+)\text{-car}@\text{(1·2)}$  are included on the top of the figure for the purpose of comparison.



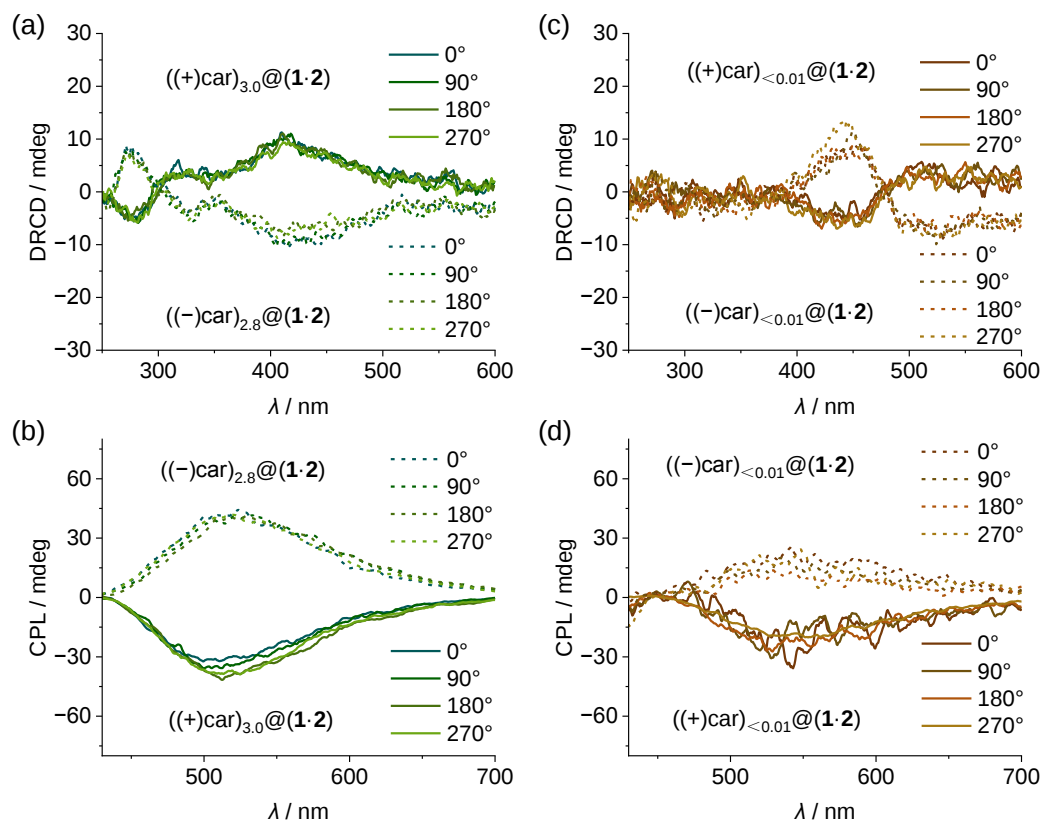
**Figure S19.** (a) DRCD, (b) CPL, (c) absorption and (d) emission spectra of the solvent-free crystal of  $(1·2)$ .



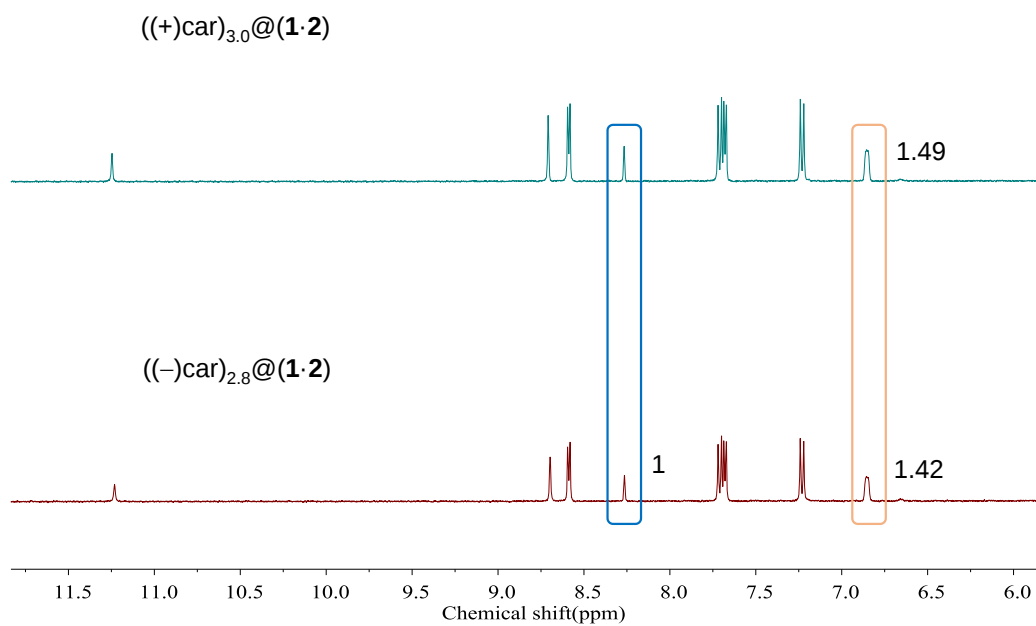
**Figure S20.** CD (upper) and UV-vis absorption (below) spectra of the solution of (a) (+)-carvone, (-)-carvone, ((+)-car)<sub>3.2</sub>@(1.2), ((-)-car)<sub>3.2</sub>@(1.2) and (1.2) and (b) ((+)-car)<sub><0.01</sub>@(1.2) and ((-)-car)<sub><0.01</sub>@(1.2) in EtOH. The solution of carvone has a concentration of  $6 \times 10^{-5}$  M.



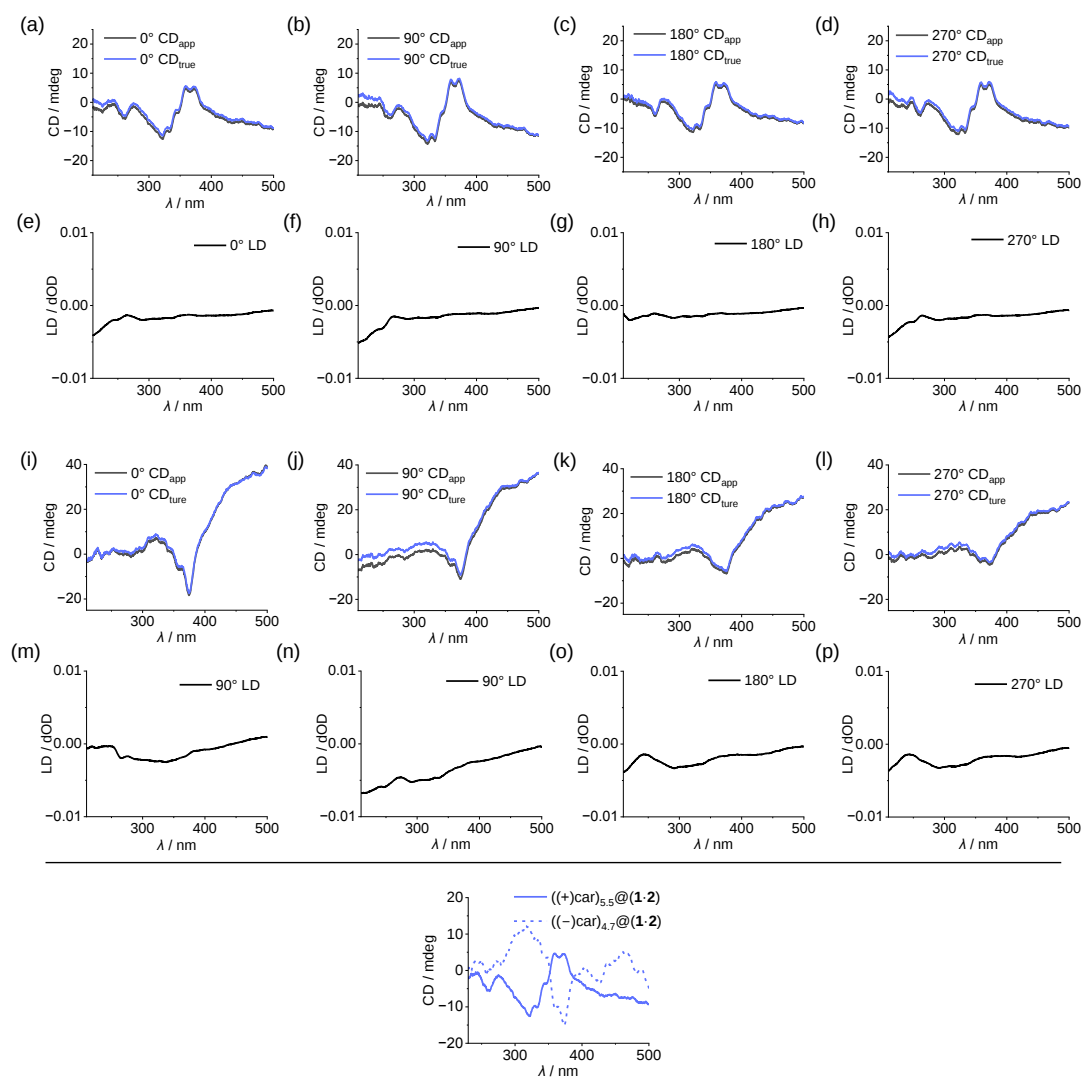
**Figure S21.** (a) DRCD, (b) absorption, (c) CPL and (d) emission spectra measured at different substrate angles from 0° to 270° of ((+)-car)<sub>0.3</sub>@(1.2), ((-)-car)<sub>0.5</sub>@(1.2).



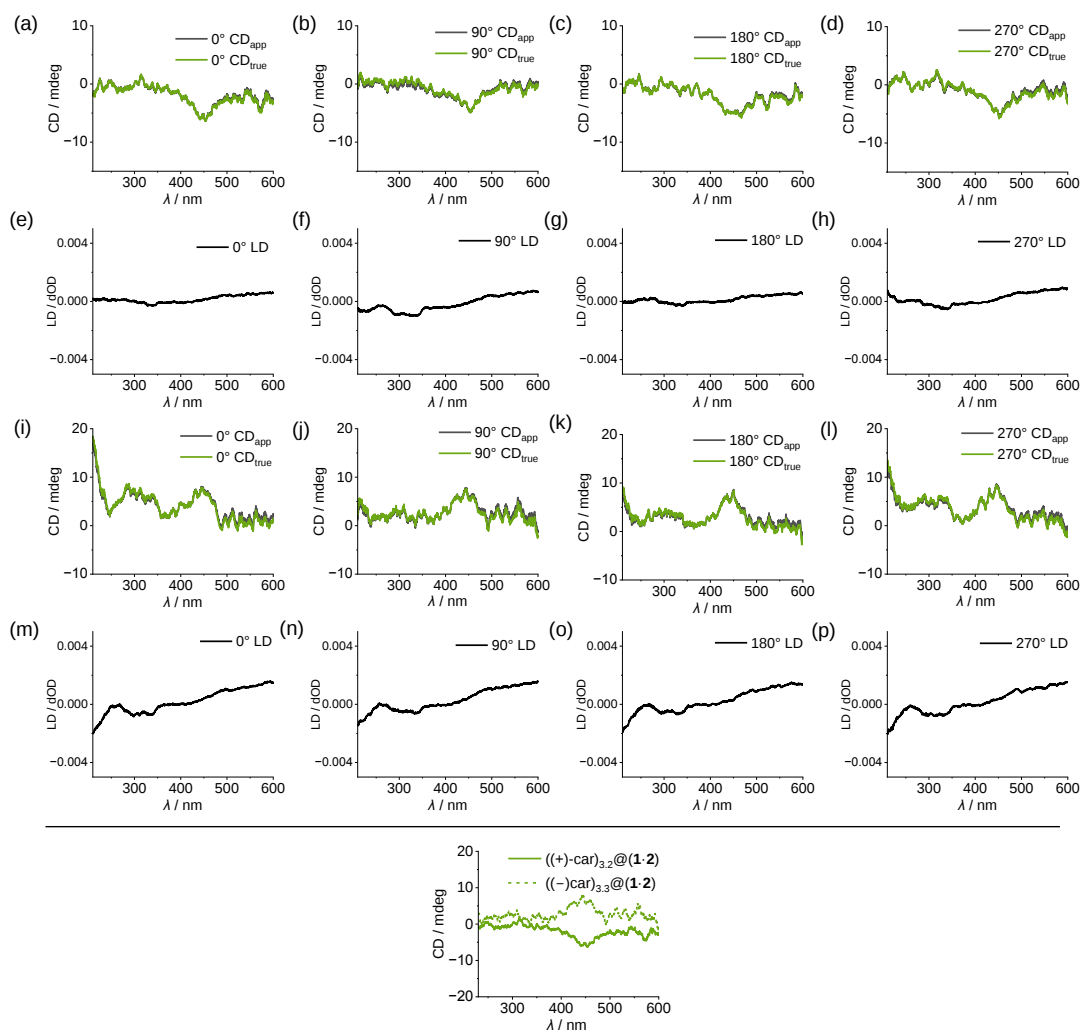
**Figure S22.** (a, c) CD and (b, d) CPL spectra of (a, b)  $((+)\text{-car})_{3.0}@\text{(1.2)}$  and  $((-)\text{-car})_{2.8}@\text{(1.2)}$  and (c, d)  $((+)\text{-car})_{<0.01}@\text{(1.2)}$  and  $((-)\text{-car})_{<0.01}@\text{(1.2)}$  after storing in a sealed tube at rt for 1 year.



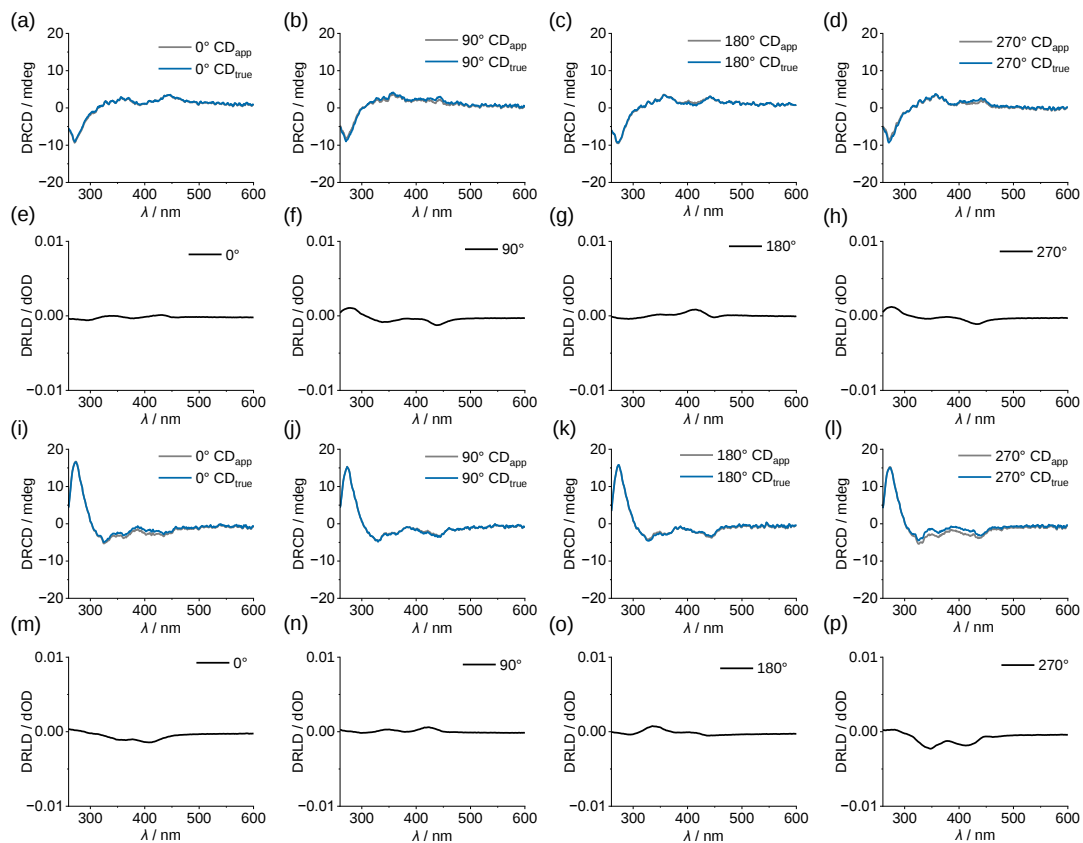
**Figure S23.**  $^1\text{H}$  NMR spectrum of  $(+)\text{car}_{3.0}@\mathbf{(1\cdot2)}$  and  $(-)\text{car}_{2.8}@\mathbf{(1\cdot2)}$  after storing in a sealed container at rt for 1 year ( $\text{DMSO-}d_6$ ). The navy-blue and orange rectangle indicates one phenyl proton of the HOF framework and one olefin proton of carvone, respectively.



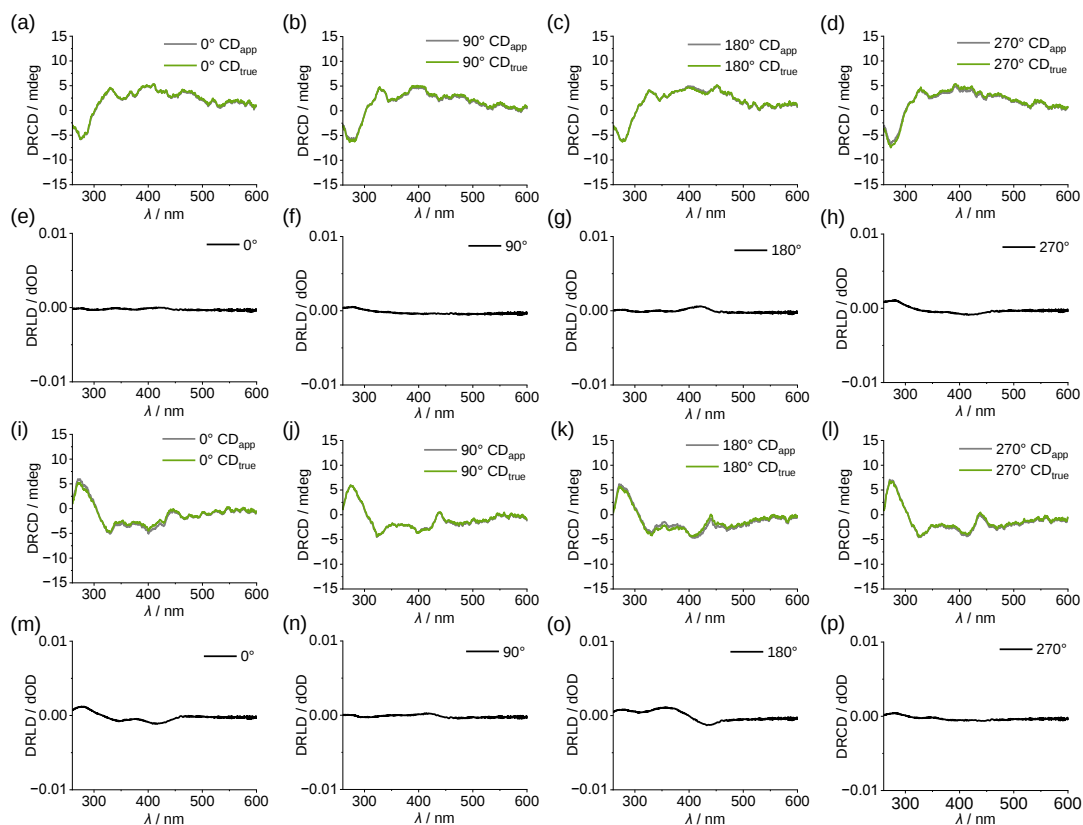
**Figure S24.** CD (upper) and relevant LD (below) spectra measured at different substrate angles from 0 ° to 270 ° of (a-h) (+)-car<sub>5,5</sub>@(1-2) and (i-p) (-)-car<sub>4,7</sub>@(1-2) microcrystals. CD spectra are measured at the transmission mode. CD<sub>app</sub> denotes the observed CD signal, CD<sub>true</sub> is the true CD signal, and LD represents the relevant linear dichroism signal. CD<sub>true</sub> were calculated according to  $CD_{true} = CD_{app} - LD \times 0.02$ .<sup>3</sup>



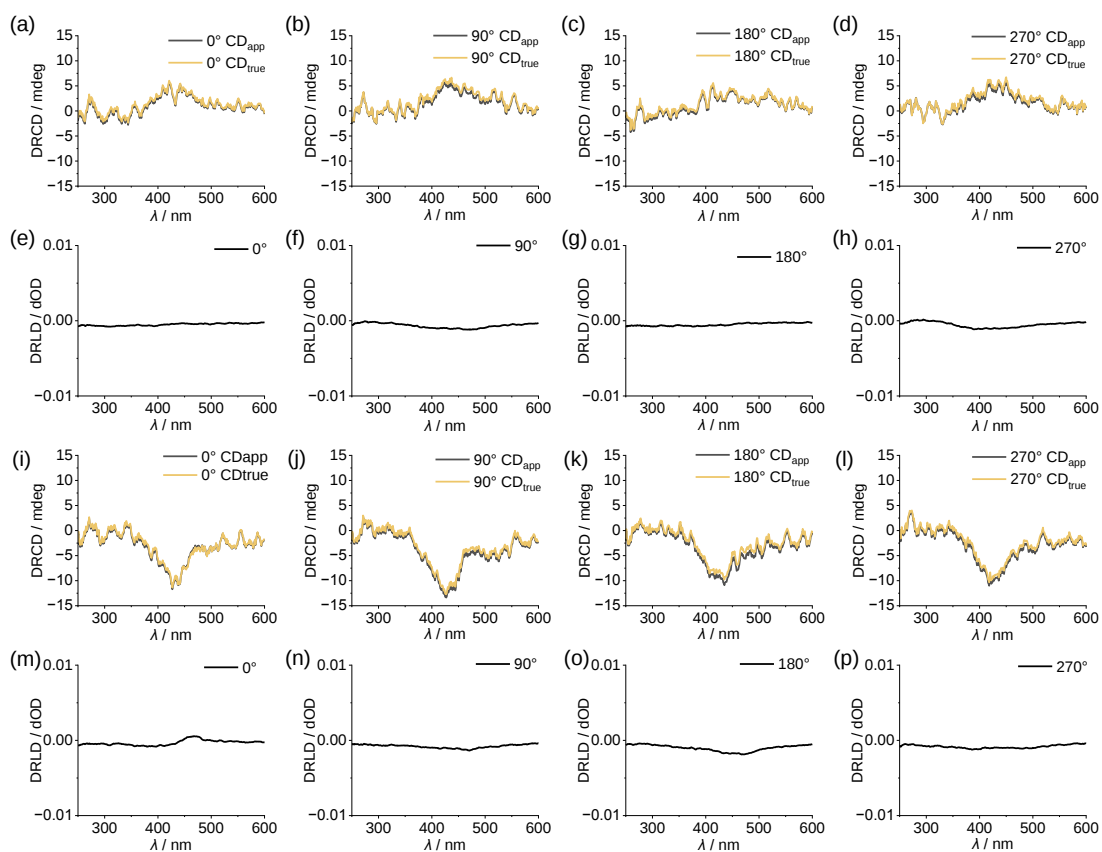
**Figure S25.** CD (upper) and relevant LD (below) spectra measured at different substrate angles from 0 °to 270 °of (a-h) ((+)-car)<sub>3,2</sub>@(1-2) and (i-p) ((-)-car)<sub>3,3</sub>@(1-2) microcrystals. CD spectra are measured at the transmission mode.



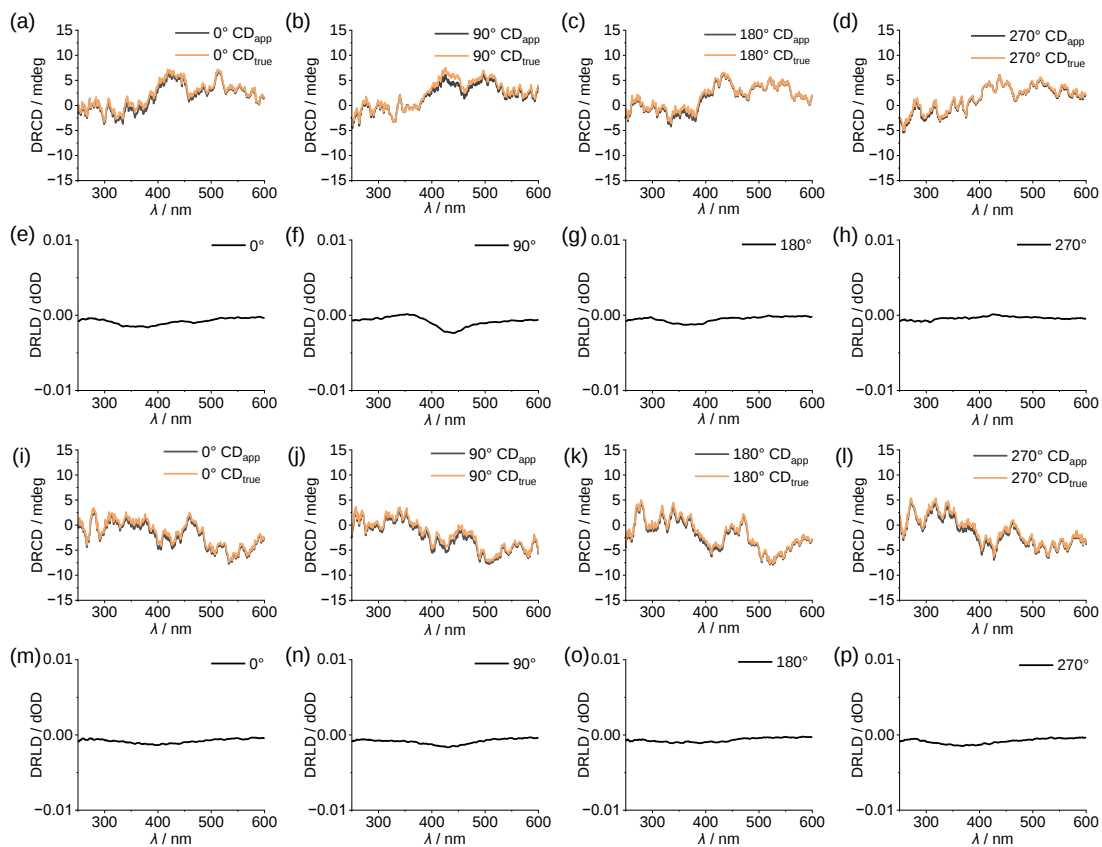
**Figure S26.** DRCD (upper) and relevant DRLD (below) spectra measured at different substrate angles from 0 ° to 270 ° of (a-h) ((+)-car)<sub>5.5</sub>@(1 2) and (i-p) ((-)-car)<sub>4.7</sub>@(1 2) microcrystals.<sup>3</sup>



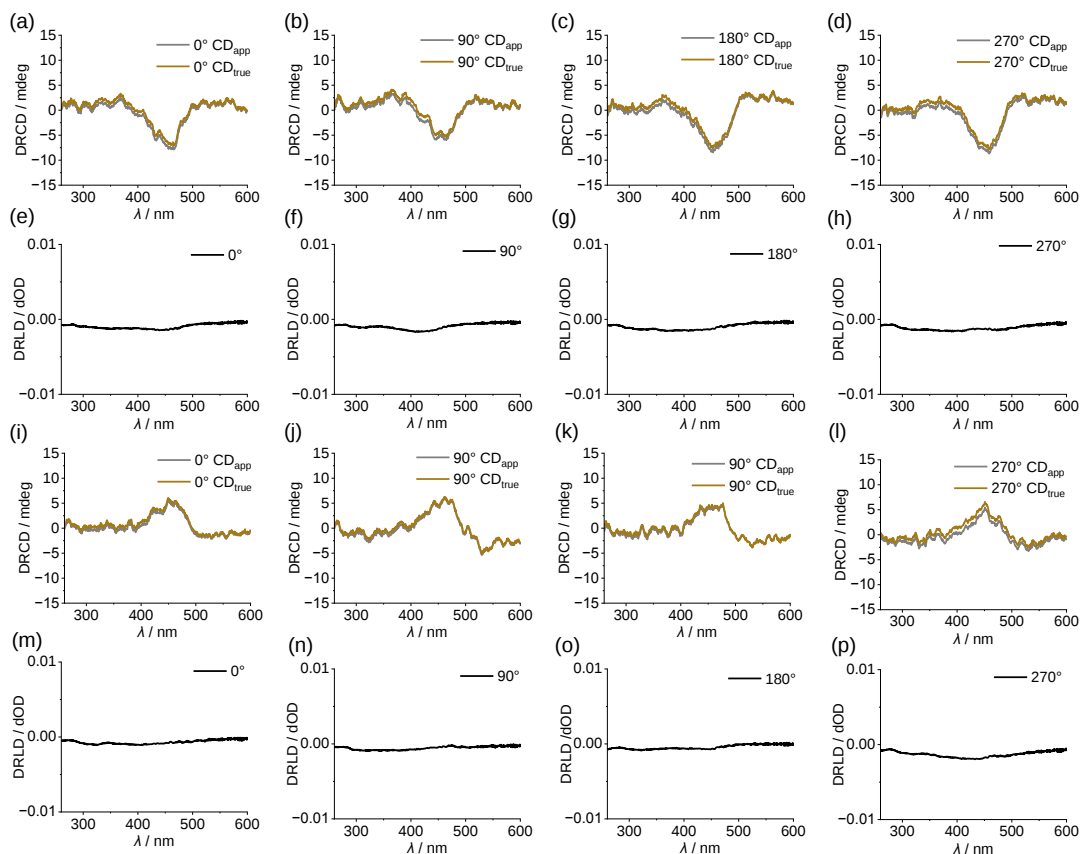
**Figure S27.** DRCD (upper) and relevant DRLD (below) spectra measured at different substrate angles from 0 ° to 270 ° of (a-h) ((+)-car<sub>3.2</sub>@(1 2)) and (i-p) ((-)-car<sub>3.3</sub>@(1 2)) microcrystals.



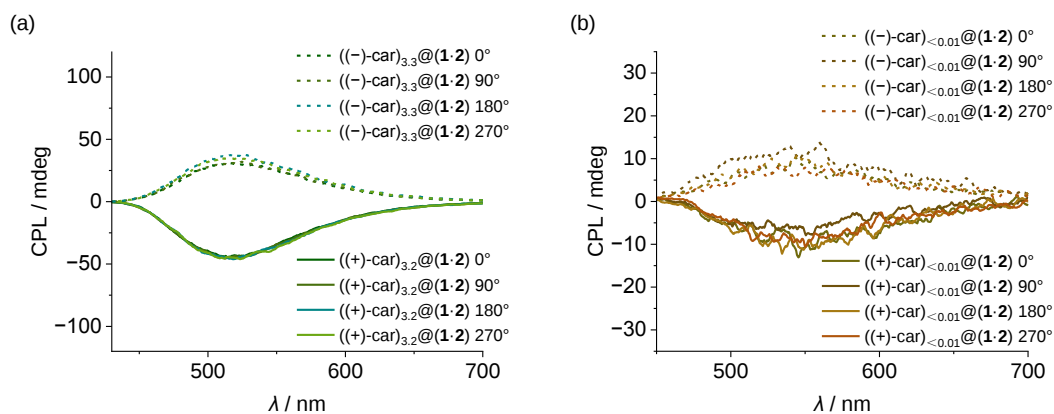
**Figure S28.** DRCD (upper) and relevant DRLD (below) spectra measured at different substrate angles from 0° to 270° of (a-h) ((+)-car)<sub>1.9</sub>@(1 2) and (i-p) ((-)-car)<sub>2.5</sub>@(1 2) microcrystals.



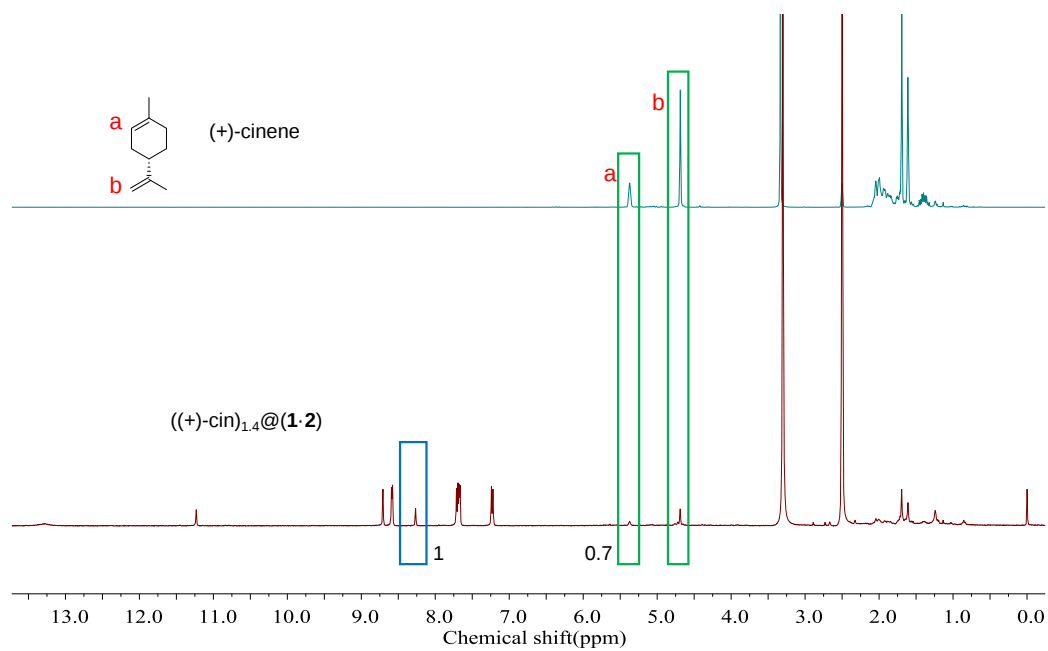
**Figure S29.** DRCD (upper) and relevant DRLD (below) spectra measured at different substrate angles from 0 ° to 270 ° of (a-h) ((+)-car)<sub>1.3</sub>@(1 2) and (i-p) ((-)-car)<sub>1.1</sub>@(1 2) microcrystals.



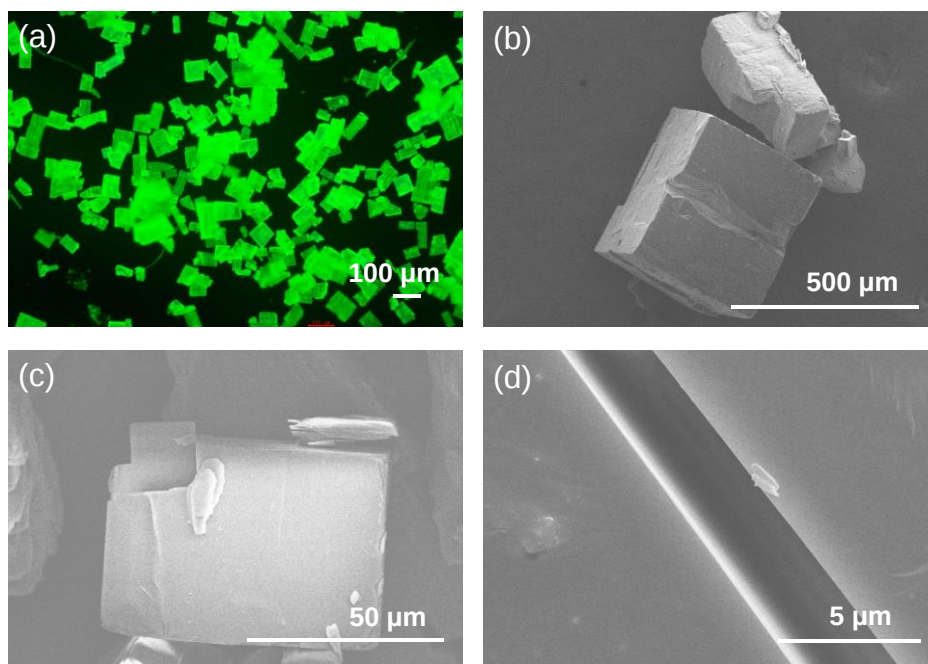
**Figure S30.** DRCD (upper) and relevant DRLD (below) spectra measured at different substrate angles from 0 ° to 270 ° of (a-h) ((+)-car)<sub><0.01<</sub>@(1 2) and (i-p) ((-)-car)<sub><0.01<</sub>@(1 2) microcrystals.



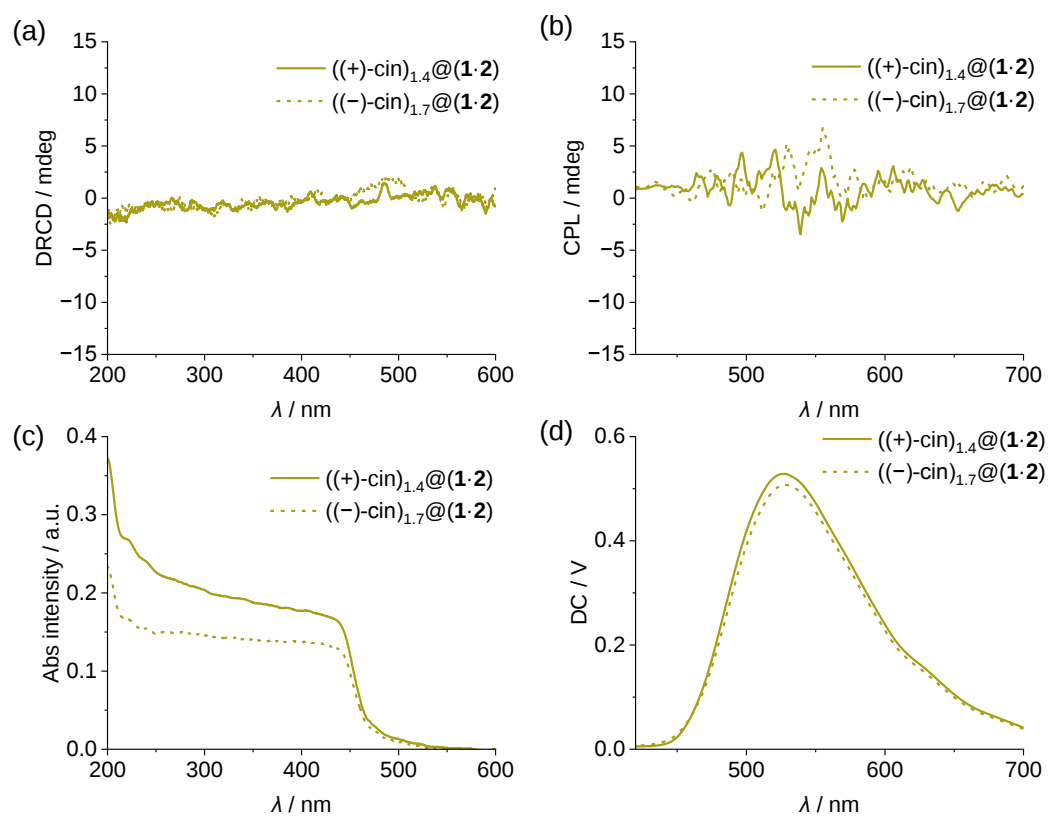
**Figure S31.** CPL spectra of (a) ((+)-car)<sub>3.2<</sub>@(1 2), ((-)-car)<sub>3.3<</sub>@(1 2) and (b) ((+)-car)<sub><0.01<</sub>@(1 2), ((-)-car)<sub><0.01<</sub>@(1 2) microcrystals measured at different substrate angles from 0 ° to 270 °.



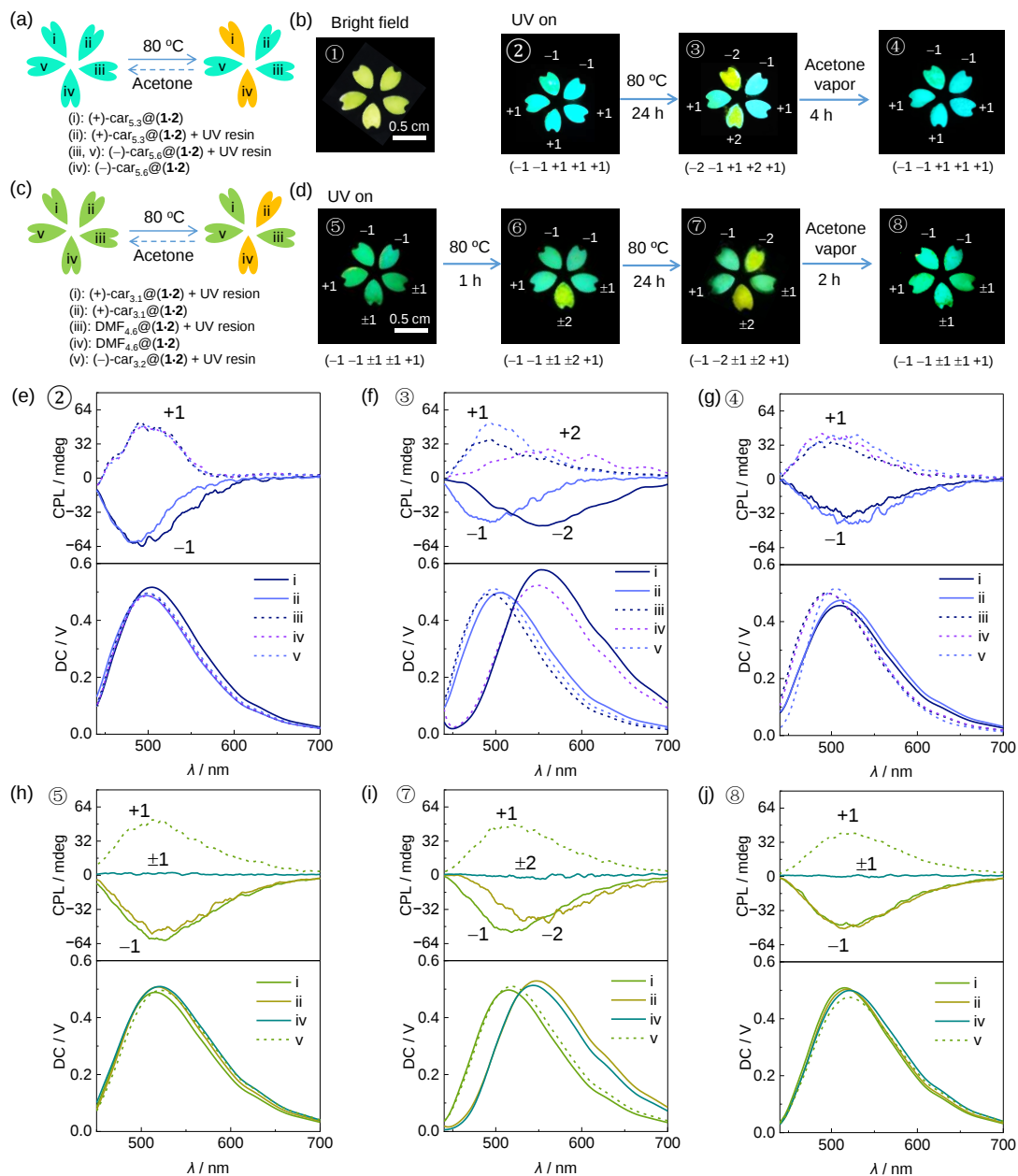
**Figure S32.**  $^1\text{H}$  NMR spectra of (+)-cinene and ((+)-cin) $_{1.4}$ @(1·2) in  $\text{DMSO-}d_6$ . The navy-blue rectangle indicates one phenyl proton of the HOF framework. The green rectangles are associated with the proton signals from cinene.



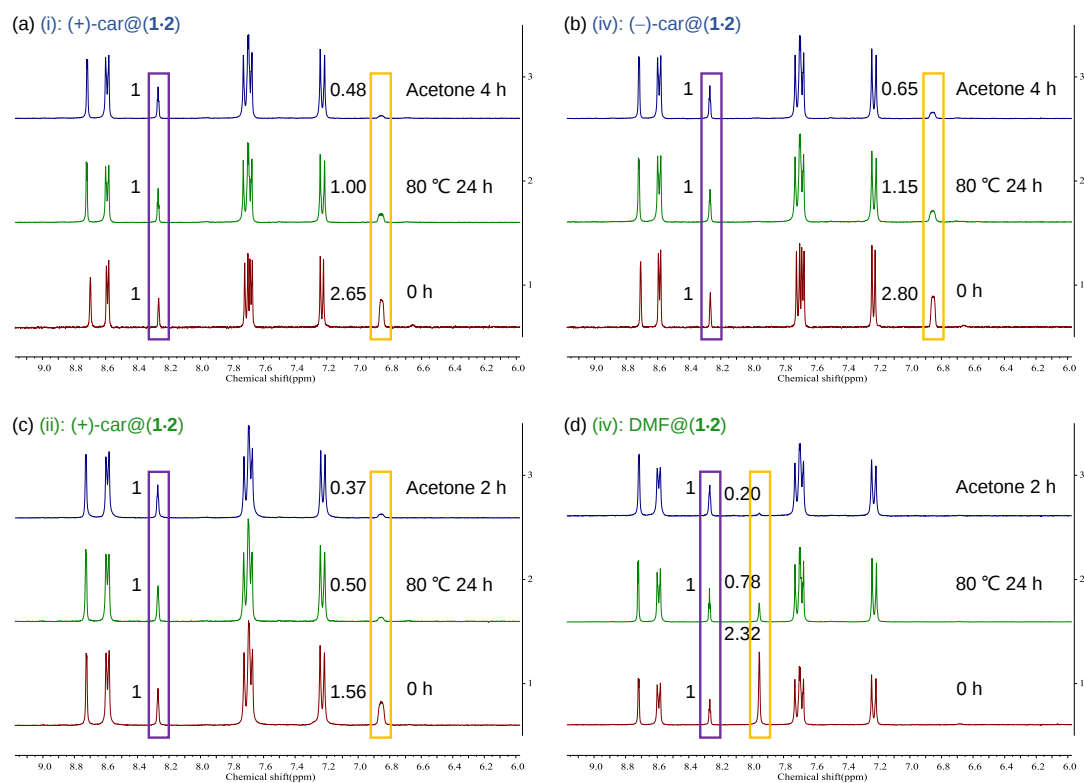
**Figure S33.** (a) Fluorescence microscopy and (b-d) SEM images of crystals of ((+)-cin) $_{1.4}$ @(1·2).



**Figure S34.** (a) DRCD, (b) CPL, (c) absorption and (d) emission spectra of the crystals of  $((+)\text{-cin})_{1.4}@\text{(1.2)}$  and  $((-)\text{-cin})_{1.7}@\text{(1.2)}$ .



**Figure S35.** (a,c) Schematic representation of a reversible process by heating and acetone-fumigating a flower pattern with five petals (i – v) consisting of different compositions of microcrystals indicated. (b,d) Images taken during the implementation of the process shown in panel (a) and (c) respectively. Each image represents a five-number code shown in the parentheses, in which each number is sequentially determined by the optical state of petal (i – v). The number –1, –2, +1, +2, ±1, ±2 represents negative cyan/green CPL, negative yellow CPL, positive cyan/green CPL, positive yellow CPL, cyan/green emission with no CPL activity, and yellow emission with no CPL activity, respectively. (e – j) CPL (upper) and DC (lower) spectra of the different petals (i – v) of the image labeled with ②, ③, ④, ⑤, ⑦, and ⑧ respectively, displayed in panel (b, d).



**Figure S36.**  $^1\text{H}$  NMR spectral changes of (a) petal (i) and (b) petal (iv) shown in panel (a/b) of Figure S35 and (c) petal (ii) and (d) petal (iv) shown in panel (c/d) of Figure S35 during the reversible encryption process. The purple and yellow rectangle indicates one phenyl proton of the HOF framework and one olefin proton of carvone (a-c) or one amino proton of DMF (d), respectively.

## References

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