Supplementary Information

Expanding the solid form landscape of Bipyridines

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Table of Contents

1. Experimental solid form screen ................................................................. 3
2. Potential energy surface scans (PES) of the carboxylic acids .................. 6
3. Representation of the experimental structures and crystal structure prediction .... 10
4. Substitution calculations ........................................................................... 21
5. Morphology of the solvates .................................................................... 23
6. Crystallographic information ..................................................................... 26
7. 2,2’-BIPY and 4,4’-BIPY Anhydrates and Hydrate .................................... 33
8. Solvates of 2,2’-BIPY and 4,4’-BIPY .......................................................... 35
9. Stability at ambient conditions .................................................................... 37
References ........................................................................................................ 41
1. Experimental solid form screen

1.1. Evaporation experiments

Fast evaporation experiments were performed by dissolving 20 mg of the anhydrate in 0.1 mL of solvent. In case the compound dissolved in the used amount the solution was directly transferred onto a watch-glass, otherwise solvent was added in 0.1 mL steps under stirring until a clear solution was obtained and the solution filtered and transferred onto the watch-glass and covered with a filter paper. The crystallization product was characterized using polarized microscopy and powder X-ray diffractometry. Few of the crystallization products showed a transformation, as indicated in Table S1 (2,2'-BIPY) and Table S2 (4,4'-BIPY).

For 2,2'-BIPY only the in the literature described anhydrate ($AH_{22}$) was obtained according to the PXRD data. However, in case of the formic acid evaporation experiment a microscopic observation of the particles confirmed that the initially formed solvate $S-C_122$ desolvated already to the anhydrate $AH_{22}$.

Table S1. Evaporation screen of 2,2'-BIPY.

| Solvent (mL) | Solid-state form | Solvent (mL) | Solid-state form |
|--------------|------------------|--------------|------------------|
| Water (3.3)  | $AH_{22}$        | Butyl acetate (0.1) | $AH_{22}$ |
| Methanol (0.1) | $AH_{12}$ | Dimethyl carbonate (0.1) | $AH_{22}$ |
| Ethanol (0.1) | $AH_{22}$ | Acetonitrile (0.1) | $AH_{22}$ |
| n-Propanol (0.1) | $AH_{22}$ | Nitromethane (0.1) | $AH_{22}$ |
| i-Propanol (0.1) | $AH_{22}$ | Dimethyl formamide (0.1) | $AH_{22}$ |
| n-Butanol (0.1) | $AH_{22}$ | Dimethyl acetamide (0.1) | $AH_{22}$ |
| t-Butanol (0.2) | $AH_{22}$ | Dimethyl sulfoxide (0.1) | $AH_{22}$ |
| n-Octanol (0.1) | $AH_{22}$ | Dichloroethane (0.1) | $AH_{22}$ |
| Ethylene glycol (0.4) | $AH_{22}$ | Chloroform (0.1) | $AH_{22}$ |
| Tetrahydrofuran (0.1) | $AH_{22}$ | Cyclohexane (0.1) | $AH_{22}$ |
| 1,4-Dioxane (0.1) | $AH_{22}$ | n-Heptane (0.4) | $AH_{22}$ |
| Diethyl ether (0.1) | $AH_{22}$ | Toluene (0.1) | $AH_{22}$ |
| Di-isopropyl ether (0.2) | $AH_{22}$ | Xylene (0.1) | $AH_{22}$ |
| Methyl-t-butyl ether (0.1) | $AH_{22}$ | Formic acid (C1) (0.1) | $AH_{22}$ |
| Acetone (0.1) | $AH_{22}$ | Acetic acid (C2) (0.1) | $S-C_122 \rightarrow AH_{22}^a$ |
| Methyl ethyl ketone (0.1) | $AH_{22}$ | Propionic acid (C3) (0.1) | $AH_{22}$ |
| Methyl isobutyl ketone (0.1) | $AH_{22}$ | Butyric acid (C4) (0.1) | $AH_{22}$ |
| Cyclohexanone (0.1) | $AH_{22}$ | Valeric acid (C5) (0.1) | $AH_{22}$ |
| Ethyl acetate (0.1) | $AH_{22}$ | Caproic acid (C6) (0.1) | $AH_{22}$ |
| i-Butyl acetate (0.1) | $AH_{22}$ | Caprylic acid (C8) (0.1) | $AH_{22}$ |

$^a$Pseudomorphosis
The majority of the 4,4′-BIPY evaporation experiments resulted in the known anhydrate form (AH$_{44}$). The evaporation experiment from water resulted in needle-shaped particles with a pronounced secondary structure due to the dehydration after removal of the mother liquor. Similar needle-shaped “pseudomorphs” were also seen together with anhydrate crystals in case of the butyl acetate, nitromethane and dichloroethane evaporation experiments, indicating that concomitant crystallization of AH$_{44}$ and Hy$_{244}$ had occurred. Evaporation experiments from formic acid (immediately measured), caproic acid and caprylic acid showed each distinct PXRD patterns. Crystals obtained from acetic acid, propionic acid, butyric acid and valeric acid were mixtures of new forms and AH$_{44}$. Thus, nine solid-state forms were identified in the 4,4′-BIPY RT watch-glass evaporation experiments.

Table S2. Evaporation screen of 4,4′-BIPY.

| Solvent (mL) | Solid-state form | Solvent (mL) | Solid-state form |
|--------------|-----------------|--------------|-----------------|
| Water (4.2)  | Hy$_{244} \rightarrow$ AH$_{44}$ | Butyl acetate (0.1) | Hy$_{244} \rightarrow$ AH$_{44}$ + AH$_{44}$ |
| Methanol (0.1) | AH$_{44}$ | Dimethyl carbonate (0.2) | AH$_{44}$ |
| Ethanol (0.1) | AH$_{44}$ | Acetonitrile (0.1) | AH$_{44}$ |
| n-Propanol (0.1) | AH$_{44}$ | Nitromethane (0.1) | Hy$_{244} \rightarrow$ AH$_{44}$ + AH$_{44}$ |
| i-Propanol (0.1) | AH$_{44}$ | Dimethyl formamide (0.1) | AH$_{44}$ |
| n-Butanol (0.1) | AH$_{44}$ | Dimethyl acetamide (0.1) | AH$_{44}$ |
| t-Butanol (0.3) | AH$_{44}$ | Dimethyl sulfoxide (0.1) | AH$_{44}$ |
| n-Octanol (0.3) | | Dichloroethane (0.1) | Hy$_{244} \rightarrow$ AH$_{44}$ + AH$_{44}$ |
| Ethylene glycol (0.2) | | Chloroform (0.1) | AH$_{44}$ |
| Tetrahydrofuran (0.1) | AH$_{44}$ | Cyclohexane (>4.2) | AH$_{44}$ |
| 1,4-Dioxane (0.1) | AH$_{44}$ | n-Heptane (4.0) | AH$_{44}$ |
| Diethyl ether (0.8) | AH$_{44}$ | Toluene (0.9) | AH$_{44}$ |
| Di-isopropyl ether (2.7) | AH$_{44}$ | Xylene (0.1) | AH$_{44}$ |
| Methyl-t-butyl ether (0.7) | AH$_{44}$ | Formic acid (C1) (0.1) | S-C$_{144}$ |
| Acetone (0.1) | AH$_{44}$ | Acetic acid (C2) (0.4) | S-C$_{244}$ |
| Methyl ethyl ketone (0.1) | AH$_{44}$ | Propionic acid (C3) (0.2) | S-C$_{344}$ |
| Methyl isobutyl ketone (0.1) | AH$_{44}$ | Butyric acid (C4) (0.4) | S-C$_{444}$ |
| Cyclohexanone (>9.5) | AH$_{44}$ | Valeric acid (C5) (0.2) | S-C$_{544}$ |
| Ethyl acetate (0.2) | AH$_{44}$ | Caproic acid (C6) (0.4) | S-C$_{644}$ |
| i-Butyl acetate (0.3) | AH$_{44}$ | Caprylic acid (C8) (>2.5) | S-C$_{844}$ |

*only needle shaped crystals showed pseudomorphosis; *no crystallization occurred within 3 months; *pseudomorphosis.

1.2. Slurry experiments in water and selected organic solvents

Slurry experiments in eleven organic solvents, chosen based on the watch-glass evaporation experiments, were performed in the temperature range between 10 and 30 °C (cycling). Samples were withdrawn periodically and analysed “wet” using PXRD. All literature forms
were confirmed and six new solvates found (one for 2,2’-BIPY and five for 4,4’-BIPY). The results are given in Table S3.

Table S3. Slurry screen of 2,2’-BIPY and 4,4’-BIPY.

| Solvent            | Solid-state form (2,2’-BIPY) | Solid-state form (4,4’-BIPY) |
|--------------------|------------------------------|------------------------------|
| Water              | AH$_{22}$                    | Hy$_{244}$                   |
| Butyl acetate      | AH$_{22}$                    | AH$_{44}$                    |
| Nitromethane       | AH$_{22}$                    | AH$_{44}$                    |
| Dichloroethane     | AH$_{22}$                    | AH$_{44}$                    |
| Formic acid (C1)   | S-C$_{122}$                  | S-C$_{144}$                  |
| Acetic acid (C2)   | AH$_{22}$                    | S-C$_{244}$                  |
| Propionic acid (C3)| AH$_{22}$                    | S-C$_{344}$                  |
| Butyric acid (C4)  | AH$_{22}$                    | S-C$_{444}$                  |
| Valeric acid (C5)  | AH$_{22}$                    | S-C$_{544}$                  |
| Caproic acid (C6)  | AH$_{22}$                    | S-C$_{644}$                  |
| Caprylic acid (C8) | AH$_{22}$                    | S-C$_{844}$                  |

1.3. Cooling crystallization experiments

The cooling crystallization screen was designed from eleven solvents that were selected based on the results of the watch-glass evaporation experiments. Hot saturated solutions of 50 – 75 mg of the compounds were prepared and then crystallization was induced by natural cooling to RT. In case of the 2,2’-isomer only the formic acid experiment resulted in a solid-state form different from the anhydrate (AH$_{22}$). For 4,4’-BIPY the limited cooling crystallization screen resulted in the hydrate (Hy$_{244}$), anhydrate (AH$_{44}$) and seven different carboxylic acid solvates (Table S4).

Table S4. Summary of cooling crystallization experiments

| Solvent            | Solid-state form (2,2’-BIPY) | Solid-state form (4,4’-BIPY) |
|--------------------|------------------------------|------------------------------|
| Water              | AH$_{22}$                    | Hy$_{244}$                   |
| Butyl acetate      | AH$_{22}$                    | AH$_{44}$                    |
| Nitromethane       | AH$_{22}$                    | AH$_{44}$                    |
| Dichloroethane     | AH$_{22}$                    | AH$_{44}$                    |
| Formic acid (C1)   | S-C$_{122}$                  | S-C$_{144}$                  |
| Acetic acid (C2)   | AH$_{22}$                    | S-C$_{244}$                  |
| Propionic acid (C3)| AH$_{22}$                    | S-C$_{344}$                  |
| Butyric acid (C4)  | AH$_{22}$                    | S-C$_{444}$                  |
| Valeric acid (C5)  | AH$_{22}$                    | S-C$_{544}$                  |
| Caproic acid (C6)  | AH$_{22}$                    | S-C$_{644}$                  |
| Caprylic acid (C8) | AH$_{22}$                    | S-C$_{844}$                  |
2. Potential energy surface scans (PES) of the carboxylic acids

PES scans were performed at the B3LYP/6-31G(d,p) level of theory using GAUSSIAN09. The dihedral angels marked in Figure S1 were scanned in 20° (1-dimensional scans) or 30° (2-dimensional) scans. Dihedral angles not scanned were optimized (extended conformation of the acid).

![Figure S1. Carboxylic acids with the for the analyses selected dihedral angles marked in green and blue (C5 only).](image)

2.1. Propionic acid (C3)

![Figure S2. Potential energy surface scan of propionic acid performed at the B3LYP/6-31G(d,p) level of theory and number of conformers found in the CSD (orange bars). Note that due to the symmetry of acid molecule most conformers are present twice in the 360° scan. Conformers were distributed uniformly, i.e. each CSD conformer is counted only once.](image)
2.2. Butyric Acid (C4)

![Graph](image1)

**Figure S3.** Potential energy surface scan of butyric acid performed at the B3LYP/6-31G(d,p) level of theory and number of conformers found in the CSD (orange bars). Note that due to the symmetry of acid molecule most conformers are present twice in the 360° scan. Conformers were distributed uniformly, i.e. each CSD conformer is counted only once.

2.3. Valeric acid (C5)

![Graph](image2)

**Figure S4.** Potential energy surface scan of valeric acid performed at the B3LYP/6-31G(d,p) level of theory and number of conformers found in the CSD (orange bars). Note that due to the symmetry of acid molecule most conformers are present twice in the 360° scan. Conformers were distributed uniformly, i.e. each CSD conformer is counted only once.
Figure S5. 2D-Potential energy surface scan of valeric acid performed at the B3LYP/6-31G(d,p) level of theory, color coded according to intramolecular energy difference with respect to the global minimum conformation (in kJ mol$^{-1}$).

2.4. Caproic acid (C6)

Figure S6. Potential energy surface scan of caproic acid performed at the B3LYP/6-31G(d,p) level of theory and number of conformers found in the CSD (orange bars). Note that due to the symmetry of acid molecule most conformers are present twice in the 360° scan. Conformers were distributed uniformly, i.e. each CSD conformer is counted only once.
2.5. **Caprylic acid (C8)**

![Graph showing potential energy surface scans of caprylic acid.](image)

**Figure S7.** Potential energy surface scans of caprylic acid performed at the B3LYP/6-31G(d,p) level of theory and number of conformers found in the CSD (orange bars). Note that due to the symmetry of acid molecule most conformers are present twice in the 360° scan. Conformers were distributed uniformly, i.e. each CSD conformer is counted only once.
3. Representation of the experimental structures and crystal structure prediction

3.1. Representation of the experimental forms

The computational models were successful in reproducing the experimental structures (Table S5). The structures were compared using the Molecular Similarity Module in Mercury to determine the root mean square deviation of the non-hydrogen atoms in a cluster of 15 molecules ($\text{rmsd}_{15}$).²

Table S5. Quality of the representation of the experimental structures of 2,2'-BIPY and 4,4'-BIPY.

| Solid Form       | Lattice parameters (cell vectors/Å, angles/°) | $\text{rmsd}_{15}$ (Å) |
|------------------|----------------------------------------------|------------------------|
|                  | $a$ / Å                                       | $b$ / Å                     | $c$ / Å                     | $\alpha$ / ° | $\beta$ / ° | $\gamma$ / ° |                      |
| **2,2'-Bipyridine** |                                              |                          |                            |              |              |              |                      |
| Anhydrate ($\text{AH}_{22}$) |                                              |                          |                            |              |              |              |                      |
| BIPYRL, P2_1/c, RT   | 5.660                                        | 6.240                     | 13.460                      | 90           | 118.73       | 90           |                      |
| BIPYRL01, P2_1/c, RT  | 5.069                                        | 6.189                     | 13.400                      | 90           | 118.80       | 90           |                      |
| BIPYRL02, P2_1/n, RT  | 11.920                                       | 6.240                     | 6.510                       | 90           | 96.40        | 90           |                      |
| BIPYRL03, P2_1/c, 110 K | 5.485(1)                                    | 6.177(1)                  | 12.356(4)                   | 90           | 110.83(1)    | 90           |                      |
| BIPYRL04, P2_1/n, 123 K | 5.486(<1)                                   | 6.166(<1)                 | 11.609(<1)                  | 90           | 95.28(<1)    | 90           |                      |
| CryOpt, P2 (P2_1/c), 0 K | 5.655                                        | 6.280                     | 13.407                      | 90           | 120.84       | 90           | 0.16                |
| PBE-TS, P2 (P2_1/c), 0 K | 5.514                                        | 6.157                     | 11.378                      | 90           | 96.69        | 90           | 0.12                |
| **Formic Acid Solvate ($\text{SC}_{12}$)** |                                              |                          |                            |              |              |              |                      |
| S-C$_{12}$, Pbc2$_1$, 173 K | 3.709(<1)                                   | 15.9139(<1)              | 19.832(<1)                  | 90           | 90           | 90           |                      |
| CryOpt, Pbc2$_1$, 0 K | 3.659                                        | 16.226                    | 19.826                      | 90           | 90           | 90           | 0.14                |
| PBE-TS, Pca2$_1$, 0 K | 15.888                                       | 3.633                     | 19.822                      | 90           | 90           | 90           | 0.05                |
| **4,4'-Bipyridine** |                                              |                          |                            |              |              |              |                      |
| Anhydrate ($\text{AH}_{34}$) |                                              |                          |                            |              |              |              |                      |
| HIQWEJ, P-1, 203 K   | 8.778 (2)                                    | 8.781(1)                  | 10.998(2)                   | 85.52(1)     | 85.42(2)     | 75.57(1)     |                      |
| HIQWEJ01, P-1, RT    | 8.830(2)                                    | 8.894(1)                  | 11.024(2)                   | 85.48(2)     | 85.41(1)     | 77.83(3)     |                      |
| HIQWEJ02, P-1, 193 K | 8.761(<1)                                   | 8.779(<1)                 | 11.011(<1)                  | 85.26(<1)    | 85.40(<1)    | 78.71(<1)    |                      |
| HIQWEJ03, P-1, 150 K | 8.693(<1)                                   | 8.735(<1)                 | 10.982(<1)                  | 85.14(<1)    | 85.37(<1)    | 78.95(<1)    |                      |
| CryOpt, P-1, 0 K    | 9.003                                        | 8.760                     | 11.072                      | 92.77        | 93.45        | 78.40        | 0.20                |
| PBE-TS, P-1, 0 K    | 8.450                                        | 8.792                     | 10.920                      | 85.79        | 85.81        | 79.66        | 0.15                |
| **Dihydrate (Hy2$_{2}$)** |                                              |                          |                            |              |              |              |                      |
| WOVYEL, P2$_1$, 130 K | 9.133 (<1)                                   | 7.431(<1)                 | 14.171(1)                   | 90           | 101.05(<1)   | 90           |                      |
| WOVYEL01, P2_1/n, RT | 9.249(1)                                    | 7.583(1)                  | 14.816(3)                   | 90           | 100.75(3)    | 90           |                      |
| WOVYEL02, P2$_1$, 93 K | 9.121(<1)                                   | 7.410(<1)                 | 14.721(<1)                  | 90           | 100.99(<1)   | 90           |                      |
| WOVYEL03, C2, 120 K | 15.816(4)                                   | 3.713(<1)                 | 9.177(2)                    | 90           | 113.71(1)    | 90           |                      |
| CryOpt, P2$_1$, 0 K | 9.504                                        | 7.254                     | 14.466                      | 90           | 102.92       | 90           | 0.26                |
| PBE-TS, P2$_1$, 0 K | 9.068                                        | 7.275                     | 14.621                      | 90           | 101.15       | 90           | 0.06                |
| **Formic Acid Solvate ($\text{SC}_{12}$)** |                                              |                          |                            |              |              |              |                      |
| GOKCEQ, P2$_1$, RT   | 3.786(5)                                    | 7.938(10)                 | 20.940(30)                  | 90           | 95.16(3)     | 90           |                      |
| CryOpt, P2$_1$, 0 K | 3.640                                        | 7.676                     | 22.339                      | 90           | 96.79        | 90           | 0.36                |
| PBE-TS, P2$_1$, 0 K | 3.615                                        | 7.926                     | 20.747                      | 90           | 94.78        | 90           | 0.11                |
| **Acetic Acid Solvate ($\text{SC}_{24}$)** |                                              |                          |                            |              |              |              |                      |
| SITDI, Pc, RT   | 3.893(2)                                    | 8.181(5)                  | 22.563(15)                  | 90           | 98.43(3)     | 90           |                      |
| CryOpt, Pc, 0 K    | 3.739                                        | 8.129                     | 23.109                      | 90           | 95.28        | 90           | 0.23                |
| PBE-TS, Pc, 0 K    | 3.693                                        | 8.191                     | 22.272                      | 90           | 91.13        | 90           | 0.12                |
| **Propionic Acid Solvate ($\text{SC}_{24}$)** |                                              |                          |                            |              |              |              |                      |
| S-C$_{24}$, P-1, 173 K | 5.218(<1)                                   | 6.269(<1)                 | 13.025(<1)                  | 96.04(<1)    | 100.82(<1)   | 103.95(<1)   |                      |
Table S5 (continued). Quality of the representation of the experimental structures of 2,2′-BIPY and 4,4′-BIPY.

| Solid Form | Lattice parameters (cell vectors/Å, angles/°) | rmsd₁₅ (Å) |
|------------|---------------------------------------------|-------------|
|            | a / Å | b / Å | c / Å | α / ° | β / ° | γ / ° |
| **Butyric Acid Solvate (S-C₄₄₄₄)*** | | | | | | |
| S-C₃₄₄₄, P-1, 173 K | 5.230(3) | 6.240(2) | 14.119(10) | 87.52(4) | 83.59(5) | 78.10(4) | 0.39 |
| CryOpt, P1 (P-1), 0 K | 5.248 | 6.223 | 14.656 | 85.52 | 81.51 | 71.70 | 0.15 |
| PBE-TS, P1 (P-1), 0 K | 5.161 | 6.198 | 13.836 | 89.25 | 83.17 | 75.72 | 0.15 |
| **Valeric Acid Solvate (S-C₅₄₄₄)*** | | | | | | |
| S-C₅₄₄₄, P-1, 173 K | 5.136(1) | 6.380(1) | 15.658(4) | 82.44(2) | 89.93(2) | 80.60(2) | 0.48 |
| CryOpt, P1 (P-1), 0 K | 5.350 | 5.876 | 16.554 | 85.71 | 90.49 | 79.42 | 0.07 |
| PBE-TS, P1 (P-1), 0 K | 5.089 | 6.354 | 15.463 | 82.39 | 89.68 | 79.73 | 0.07 |
| **Caproic Acid Solvate (S-C₆₄₄₄)*** | | | | | | |
| S-C₆₄₄₄, P-1, 173 K | 5.021(<1) | 6.654(1) | 16.974(2) | 100.65(1) | 93.11(1) | 97.62(1) | 0.73 |
| CryOpt, P1 (P-1), 0 K | 5.064 | 6.856 | 15.662 | 102.18 | 96.57 | 96.14 | 0.45 |
| PBE-TS, P1 (P-1), 0 K | 5.237 | 7.445 | 14.784 | 103.94 | 95.38 | 95.23 | 0.21 |
| **Caprylic Acid Solvate (S-C₈₄₄₄)*** | | | | | | |
| S-C₈₄₄₄, P-1, 173 K | 8.911(<1) | 9.630(1) | 16.471(<1) | 99.00(1) | 93.96(1) | 113.38(1) | 0.11 |
| CryOpt, P1 (P-1), 0 K | 8.998 | 9.828 | 16.521 | 100.07 | 94.32 | 112.10 | 0.11 |
| PBE-TS, P1 (P-1), 0 K | 8.924 | 9.493 | 16.166 | 100.38 | 93.73 | 114.09 | 0.11 |

Figure S8. Overlay of the 15-molecule cluster of the observed structure of AH₂₂ (BIPYRL04₃, colored by element) and calculated PBE-TS structure (green), rmsd₁₅=0.12 Å.

Figure S9. Overlay of the 15-molecule cluster of the observed structure of AH₄₄ (HIQWEJ02₄, colored by element) and calculated PBE-TS structure (green), rmsd₁₅=0.15 Å.
Figure S10. Overlay of the 15-molecule cluster of the observed structure of \textbf{Hy2}_{44} (WOVYELO2$^5$), colored by element) and calculated PBE-TS structure (green), $rmsd_{15}=0.06$ Å.

Figure S11. Overlay of the 15-molecule cluster of the observed structure of \textbf{S-C1}_{22} (colored by element) and calculated PBE-TS structure (green), $rmsd_{15}=0.05$ Å.

Figure S12. Overlay of the 15-molecule cluster of the observed structure of \textbf{S-C1}_{44} (GOKCEO$^6$, colored by element) and calculated PBE-TS structure (green), $rmsd_{15}=0.11$ Å.
**Figure S13.** Overlay of the 15-molecule cluster of the observed structure of S-C244 (SITDJ, colored by element) and calculated PBE-TS structure (green), $rmsd_{15}=0.12$ Å.

**Figure S14.** Overlay of the 15-molecule cluster of the observed structure of S-C344 (colored by element, main disorder component only) and calculated PBE-TS structure (green), $rmsd_{15}=0.13$ Å.

**Figure S15.** Overlay of the 15-molecule cluster of the observed structure of S-C444 (colored by element) and calculated PBE-TS structure (green), $rmsd_{15}=0.15$ Å.
**Figure S16.** Overlay of the 15-molecule cluster of the observed structure of **S-C5**44 (colored by element) and calculated PBE-TS structure (green), $rmsd_{15}=0.07$ Å.

**Figure S17.** Overlay of the 15-molecule cluster of the observed structure of **S-C6**44 (one disorder component only, colored by element) and calculated PBE-TS structure (green), $rmsd_{15}=0.45$ Å.

**Figure S18.** Overlay of the 15-molecule cluster of the observed structure of **S-C8**44 (colored by element) and calculated PBE-TS structure (green), $rmsd_{15}=0.11$ Å.
### 3.2. Computational generation of low-energy structures

Table S6 provides an overview over the number of structures and energy ranges of the structures selected to be generated/optimized at the different stages of the generation of the lattice energy landscapes.

**Table S6. Overview Computational Generation of the Anhydrate Crystal Energy Landscapes.**

|                     | 2,2'-Bipyridine (Z'=1) | 4,4'-Bipyridine (Z'=1) | 4,4'-Bipyridine (Z'=2) |
|---------------------|------------------------|------------------------|------------------------|
| **CrystalPredictor (rigid body)** |                        |                        |                        |
| Charges             | PBE0/aug-cc-pVTz        | PBE0/aug-cc-pVTz        | PBE0/aug-cc-pVTz        |
| Number of structures| 500000                 | 1000000                | 1000000                |
| **DMACRYS (rigid body)** |                        |                        |                        |
| Multipoles          | PBE0/aug-cc-pVTz        | PBE0/aug-cc-pVTz        | PBE0/aug-cc-pVTz        |
| Energy range        | 19 kJ mol⁻¹             | 19 kJ mol⁻¹ (Z'=1)      | 19 kJ mol⁻¹             |
| Number of structures| 15107                  | 12784                  | 10002                  |
| **CrystalOptimizer (flexible)** |                      |                        |                        |
| Multipoles          | PBE0/aug-cc-pVTz        | PBE0/aug-cc-pVTz        | PBE0/aug-cc-pVTz        |
| Energy range        | 7.5 kJ mol⁻¹            | 7.5 kJ mol⁻¹            | 7.5 kJ mol⁻¹            |
| Number of structures| 197                    | 88                     | 91                     |
| **CASTEP PBE-TS (cut-off: 780 eV, k-points: 0.07)** |       |                        |                        |
| Energy range        | 5 kJ mol⁻¹              | 7.5 kJ mol⁻¹            | 7.5 kJ mol⁻¹            |
| Number of structures| 60                     | 40                     | 31                     |
| **CASTEP PBE-MBD* (cut-off: 1100 eV, k-points: 0.07, single point calculations)** | | | |
| Energy range        | 7.5 kJ mol⁻¹            | 7.5 kJ mol⁻¹            | 7.5 kJ mol⁻¹            |
| Number of structures| 31                     | 25                     | 8                      |
The lowest-energy PBE-TS structures of 2,2’-BIPY and 4,4’-BIPY are given in Tables S6 and S7, respectively.

**Table S7.** Computationally generated low-energy 2,2’-BIPY PBE-TS structures. The experimental structure is highlighted in grey.

| Str.× | Space group      | a/Å | b/Å | c/Å | α/° | β/° | γ/° | E_{last}/kJ mol⁻¹ | PⅢ | E_{cluster(15)}/kJ mol⁻¹ |
|-------|------------------|-----|-----|-----|-----|-----|-----|-------------------|-----|------------------------|
| 204   | P2₁/n (0.5)      | 5.514 | 6.157 | 11.378 | 90 | 96.69 | 90 | -137.04 | 0.757 | -85.4 |
| 966   | P2₁/n (0.5)      | 3.713 | 9.135 | 11.215 | 90 | 95.05 | 90 | -134.77 | 0.764 | -80.2 |
| 503   | P2₁/n (1)        | 5.805 | 11.142 | 11.916 | 90 | 90.35 | 90 | -133.47 | 0.752 | -77.65 |
| 240   | P2₁/n (1)        | 6.795 | 10.977 | 10.670 | 90 | 101.57 | 90 | -132.55 | 0.744 | -84.2 |
| 35    | Pna₂₁ (1)        | 17.992 | 3.724 | 11.409 | 90 | 90 | 90 | -132.17 | 0.764 | -77.4 |
| 118   | P₂₁/c (0.5)      | 3.723 | 9.483 | 11.008 | 90 | 99.32 | 90 | -134.09 | 0.756 | -78 |
| 299   | Pbca (1)         | 5.983 | 12.301 | 21.143 | 90 | 90 | 90 | -133.92 | 0.747 | -80.7 |
| 877   | P₂₁/n (0.5)      | 5.770 | 11.786 | 6.157 | 90 | 109.22 | 90 | -133.81 | 0.735 | -82.9 |
| 3751  | P₂₁/n (1)        | 5.044 | 13.211 | 11.754 | 90 | 96.79 | 90 | -132.73 | 0.746 | -79.5 |
| 244   | C2/c (1)         | 19.643 | 5.951 | 13.369 | 90 | 94.90 | 90 | -132.54 | 0.745 | -80.05 |
| 175   | P₂₁/c (0.5)      | 3.734 | 9.645 | 10.798 | 90 | 94.09 | 90 | -132.40 | 0.754 | -75.3 |
| 1050  | P₂₁/n (1)        | 5.647 | 11.954 | 11.566 | 90 | 98.41 | 90 | -132.10 | 0.751 | -77.2 |
| 570   | P₂₁₂₁,2₁ (1)     | 3.720 | 9.048 | 22.695 | 90 | 90 | 90 | -132.10 | 0.763 | -76.6 |
| 3011  | P₂₁₂₁,2₁ (1)     | 7.393 | 9.981 | 10.675 | 90 | 90 | 90 | -131.62 | 0.743 | -82.4 |
| 1759  | Pbca (1)         | 11.684 | 10.657 | 12.575 | 90 | 90 | 90 | -131.61 | 0.741 | -81.15 |
| 12    | Pna₂₁ (1)        | 13.605 | 4.977 | 11.669 | 90 | 90 | 90 | -131.52 | 0.737 | -78 |
| 419   | Pca₂₁ (1)        | 23.115 | 3.705 | 9.092 | 90 | 90 | 90 | -131.49 | 0.750 | -76.4 |
| 128   | P₂₁₂₁,2₁ (1)     | 5.086 | 11.739 | 13.094 | 90 | 90 | 90 | -131.43 | 0.745 | -78.6 |
| 1132  | P₂₁/n (1)        | 5.659 | 9.271 | 14.773 | 90 | 92.67 | 90 | -131.29 | 0.750 | -77.7 |
| 1807  | C2/c (1)         | 10.627 | 8.572 | 17.519 | 90 | 105.46 | 90 | -131.17 | 0.755 | -78.05 |
| 435   | I2/c (1)         | 11.218 | 11.421 | 13.212 | 90 | 113.51 | 90 | -130.99 | 0.745 | -76.7 |
| 65    | Pna₂₁ (1)        | 18.572 | 3.742 | 11.105 | 90 | 90 | 90 | -130.87 | 0.756 | -75.3 |
| 100   | P₂₁/n (1)        | 3.726 | 9.036 | 23.024 | 90 | 92.75 | 90 | -130.81 | 0.749 | -75.25 |
| 654   | P₂₁/n (1)        | 5.744 | 11.130 | 12.375 | 90 | 98.6 | 90 | -130.78 | 0.744 | -77.5 |
| 1514  | Pca₂₁ (1)        | 11.413 | 9.284 | 7.415 | 90 | 90 | 90 | -130.78 | 0.742 | -82.2 |
| 699   | Aba₂ (1)         | 22.950 | 6.969 | 9.863 | 90 | 90 | 90 | -130.61 | 0.737 | -80.55 |
| 627   | P₂₁₂₁,2₁ (1)     | 5.185 | 10.519 | 14.463 | 90 | 90 | 90 | -130.57 | 0.741 | -79.7 |
| 539   | P₂₁/c (1)        | 10.749 | 6.314 | 12.177 | 90 | 106.65 | 90 | -130.35 | 0.733 | -81.6 |
| 253   | P₂₁/n (1)        | 7.208 | 9.501 | 11.689 | 90 | 104.30 | 90 | -130.10 | 0.746 | -77.45 |
| 1292  | P₂₁/c (1)        | 9.205 | 11.635 | 7.339 | 90 | 96.81 | 90 | -129.96 | 0.742 | -79.25 |
| 1805  | P₂₁₂₁,2₁ (1)     | 6.395 | 10.951 | 11.520 | 90 | 90 | 90 | -129.79 | 0.713 | -79.7 |

×Structure ID: CrystalPredictor rank; ⅢPacking Index calculated using PLATON®; ⅢCalculated using Crystal Explorer (see manuscript section 2.3).
| Str.* | Space group (Z') | Cell parameters | E_int/ E_cluster/ | E_int/ | E_cluster/ |
|-------|------------------|-----------------|-------------------|--------|-----------|
|       |                  | a/Å  b/Å  c/Å  a'/Å  b'/Å  c'/Å | kJ mol⁻¹ | kJ mol⁻¹ |
| 1333  | P4_2_2_2 (0.25)  | 10.447 10.447 3.633 90 90 90 | -147.53 | 0.726 | -83.90     |
| 1149  | Pbcn (1)         | 7.149 11.424 18.420 90 90 90 | -147.29 | 0.773 | -96.05     |
| 8319  | I222 (0.25)      | 3.658 5.783 17.895 90 90 90 | -146.13 | 0.762 | -77.26     |
| 1874  | C2/c (1)         | 18.773 3.663 22.765 90 106.14 90 | -145.67 | 0.774 | -82.13     |
| 5529  | C2/c (0.5)       | 18.786 3.661 11.210 90 103.90 90 | -145.26 | 0.778 | -86.50     |
| 7291  | Pbcn (0.5)       | 3.659 11.220 18.166 90 90 90 | -144.70 | 0.776 | -86.60     |
| 862   | Pbcn (2)         | 18.425 7.115 23.227 90 90.00 90 | -144.53 | 0.765 | -93.30     |
| 6367  | C2/c (0.5)       | 6.382 18.476 6.983 90 115.12 90 | -144.10 | 0.768 | -96.10     |
| 648b  | Pbcn (2)         | 7.143 11.564 36.738 90 90.00 90 | -144.09 | 0.766 | -94.40     |
| 7091  | P2_1/c (2)       | 14.809 3.631 29.920 90 91.75 90 | -143.78 | 0.715 | -82.73     |
| 1476  | C2/c (0.5)       | 11.771 5.883 11.503 90 105.55 90 | -143.67 | 0.755 | -91.60     |
| 379   | P21/c (0.5)      | 8.906 5.612 7.480 90 95.00 90 | -143.58 | 0.777 | -95.20     |
| 2471  | P-1 (2)          | 8.557 8.583 10.958 85.18 85.31 80.08 | -143.55 | 0.732 | -93.43     |
| 67    | C2/c (1)         | 16.924 5.895 16.674 90 113.2 90 | -143.54 | 0.758 | -89.10     |
| 9284  | Pbcn (2)         | 14.648 11.278 18.395 90 90 90 | -143.50 | 0.767 | -85.95     |
| 125   | P2_1/n (0.5)     | 3.773 5.495 17.987 90 94.84 90 | -143.10 | 0.776 | -82.00     |
| 763   | I2/a (1)         | 7.421 5.740 35.475 90 94.58 90 | -143.01 | 0.772 | -82.73     |
| 84    | Pbcn (0.5)       | 5.854 18.532 7.096 90 90 90 | -142.80 | 0.749 | -90.60     |
| 7646  | P2_1/n (1)       | 12.467 3.718 16.268 90 99.16 90 | -142.39 | 0.776 | -89.50     |
| 6531  | P2_1/c (1)       | 3.659 5.779 36.016 90 90.75 90 | -142.18 | 0.761 | -76.50     |
| 692   | Cc (2)           | 7.203 5.850 9.039 90 97.65 90 | -142.04 | 0.777 | -81.98     |
| 771   | I2/c (1)         | 7.303 5.648 18.490 90 100.49 90 | -141.90 | 0.771 | -91.40     |
| 1313  | I2/a (1)         | 19.329 3.650 22.651 90 110.20 90 | -141.80 | 0.769 | -87.10     |
| 78    | P2_1/c (1)       | 9.883 7.055 11.732 90 110.78 90 | -141.60 | 0.759 | -91.95     |
| 312   | P2_1/n (1)       | 8.037 5.717 16.403 90 94.09 90 | -141.41 | 0.771 | -95.50     |
| 179   | P2_1/c (1)       | 9.664 10.765 7.700 90 100.60 90 | -141.30 | 0.736 | -91.65     |
| 8367  | Pbcn (1)         | 5.876 7.109 36.550 90 90 90 | -141.29 | 0.761 | -86.60     |
| 1631  | P2_1/n (2)       | 9.712 7.021 22.546 90 95.75 90 | -141.24 | 0.759 | -91.60     |
| 1383  | C2/c (1)         | 18.437 5.756 14.572 90 101.19 90 | -141.21 | 0.764 | -88.85     |
| 2249  | Pcab (2)         | 18.446 6.993 23.737 90 90 90 | -140.97 | 0.757 | -91.68     |
| 1532  | C222 (0.5)       | 5.634 18.589 7.188 90 90 90 | -140.74 | 0.766 | -90.20     |
| 268   | P2_1/c (1)       | 10.048 6.170 13.016 90 109.67 90 | -140.45 | 0.766 | -90.35     |
| 8415  | Pbcn (0.5)       | 5.813 7.175 18.235 90 90 90 | -140.21 | 0.744 | -86.90     |

*Structure ID: CrystalPredictor rank; *Packing Index calculated using PLATON; * Calculated using Crystal Explorer (see manuscript section 2.3).
3.3. Structure family similarity trees and Packing comparisons

The structure family similarity trees were calculated using the CCDC API packing similarity dendrogram script with clustering type settings “complete”.

Figure S19. Structure family similarity tree, showing the crystal packing similarity between the lowest-energy crystal structures from the 2,2'-BIPY CSP search. Experimental structure: 204.
Figure S20. Packing comparisons of selected 2,2'-BIPY structures. Missed matches are shown in red.

(a) 204 (AH22) and 299 (rmsd$_{11}$ = 0.15 Å)  
(b) 204 (AH22) and 539 (rmsd$_{11}$ = 0.26 Å)

Figure S21. Structure family similarity tree, showing the crystal packing similarity between the lowest-energy crystal structures from the 4,4'-BIPY CSP searches. Experimental structure: 2471.
Figure S22. Packing comparisons of selected 4,4'-Bipy structures. Missed matches are shown in red. Note that one layer is identical for all structures.
4. Substitution calculations

Substitution calculations were performed to investigate the potential of isostructural solvates.

The acetic acid molecule was pasted into the S-C144 structure (P2₁) and optimized with CASTEP as described in the manuscript in section 2.2. The obtained structure was calculated to be 0.71 kJ mol⁻¹ less stable in lattice energy. An overlay of S-C144 and the hypothetical P2₁ structure is given in Figure S23.

![Figure S23](image)

**Figure S23.** Overlay of S-C2₄₄ (colored by element) and a hypothetical P2₁ acetic acid solvate structure (green, isostructural with S-C1₄₄), viewed along the (a) a and (b) b crystallographic axes.

Similarly, the acetic acid molecule was pasted into the triclinic 4,4'-BIPY solvate structures (S-C3₄₄, S-C4₄₄, S-C5₄₄, S-C6₄₄ and S-C8₄₄). The isomorphous acetic acid solvates were calculated to be higher in lattice energy: in S-C3₄₄ +14.88 kJ mol⁻¹, in S-C4₄₄ +30.39 kJ mol⁻¹ and other solvate structures even less stable.
The .res file for the P2₁ acetic acid solvate structure is given below:

| Title          | Value   |
|----------------|---------|
| TITL S-C2-44 in S-C1-44        |         |
| CELL 0.71073 3.7256 8.0602 22.4415 90 90.775 90 |         |
| ZERR 2 0.0000 0.0000 0.0000 0 0.000 0 |         |
| LATT -1 |         |
| SYMM -x,1/2+y,-z |         |
| SFAC C H N O |         |
| UNIT 28 32 4 8 |         |
| FVAR 1.00 |         |

### Atomic Coordinates

| Atom | Type | X       | Y       | Z       | Temp | Charge |
|------|------|---------|---------|---------|------|--------|
| C1   | 1    | 0.382840| 0.560000| 0.195490| 1.000000| 0.050000|
| C2   | 1    | 0.600760| 0.292900| 0.227810| 1.000000| 0.050000|
| C3   | 1    | 0.458390| 0.449310| 0.241410| 1.000000| 0.050000|
| C4   | 1    | 0.655770| 0.254720| 0.167680| 1.000000| 0.050000|
| C5   | 1    | 0.574220| 0.373780| 0.124810| 1.000000| 0.050000|
| C6   | 1    | 0.789570| -0.104350| 0.311800| 1.000000| 0.050000|
| C7   | 1    | 0.685100| 0.001900| 0.265950| 1.000000| 0.050000|
| C8   | 1    | 0.697400| 0.173820| 0.275420| 1.000000| 0.050000|
| C9   | 1    | 0.914210| 0.115100| 0.374710| 1.000000| 0.050000|
| C10  | 1    | 0.185780| 0.891920| 0.080940| 1.000000| 0.050000|
| C11  | 1    | 0.097620| 1.019020| 0.033730| 1.000000| 0.050000|
| C12  | 1    | 0.255510| 0.607870| 0.424670| 1.000000| 0.050000|
| C13  | 1    | 0.409500| 0.492300| 0.470980| 1.000000| 0.050000|

### Hydrogen Coordinates

| Atom | Type | X       | Y       | Z       | Temp | Charge |
|------|------|---------|---------|---------|------|--------|
| H1   | 2    | 0.269660| 0.682770| 0.203680| 1.000000| 0.060000|
| H2   | 2    | 0.402370| 0.484660| 0.287210| 1.000000| 0.060000|
| H3   | 2    | 0.772200| 0.136120| 0.154690| 1.000000| 0.060000|
| H4   | 2    | 0.617460| 0.349120| 0.077630| 1.000000| 0.060000|
| H5   | 2    | 0.787660| -0.238850| 0.306520| 1.000000| 0.060000|
| H6   | 2    | 0.594350| -0.048610| 0.223380| 1.000000| 0.060000|
| H7   | 2    | 0.837050| 0.361900| 0.341380| 1.000000| 0.060000|
| H8   | 2    | 1.010670| 0.155280| 0.418510| 1.000000| 0.060000|
| H9   | 2    | 0.386170| 0.667390| 0.092220| 1.000000| 0.075000|
| H10  | 2    | 0.342030| 1.069650| 0.014040| 1.000000| 0.075000|
| H11  | 2    | -0.057630| 0.960990| -0.002470| 1.000000| 0.075000|
| H12  | 2    | -0.056650| 1.121610| 0.052130| 1.000000| 0.075000|
| H13  | 2    | 0.031870| 0.827100| 0.411950| 1.000000| 0.075000|
| H14  | 2    | 0.193020| 0.421170| 0.491670| 1.000000| 0.075000|
| H15  | 2    | 0.548490| 0.560860| 0.506420| 1.000000| 0.075000|
| H16  | 2    | 0.592020| 0.403470| 0.450610| 1.000000| 0.075000|

### Nitrogen Coordinates

| Atom | Type | X       | Y       | Z       | Temp | Charge |
|------|------|---------|---------|---------|------|--------|
| N1   | 3    | 0.442600| 0.524190| 0.138040| 1.000000| 0.050000|
| N2   | 3    | 0.902520| -0.049120| 0.365260| 1.000000| 0.050000|

### Oxygen Coordinates

| Atom | Type | X       | Y       | Z       | Temp | Charge |
|------|------|---------|---------|---------|------|--------|
| O1   | 4    | 0.348740| 0.759200| 0.058980| 1.000000| 0.050000|
| O2   | 4    | 0.113160| 0.909430| 0.133890| 1.000000| 0.050000|
| O3   | 4    | 0.129340| 0.748040| 0.446970| 1.000000| 0.050000|
| O4   | 4    | 0.240480| 0.573690| 0.371170| 1.000000| 0.050000|

END
5. **Morphology of the solvates**

The morphologies of the solvates were recorded using an Olympus SZX12 stereo-microscope equipped with an Olympus DP71 digital camera (Olympus, A).

5.1. **2,2’-Bipyridine formic acid solvate**

![Photographs of S-C122](image1.png)

**Figure S24.** Photographs of S-C122. The thin crystals crystallized during taking the photographs (solvent evaporation).

5.2. **4,4’-Bipyridine formic acid solvate**

![Photographs of S-C144](image2.png)

**Figure S25.** Photographs of S-C144. Crystal on the right already started to desolvate.

5.3. **4,4’-Bipyridine acetic acid solvate**

![Photographs of S-C244](image3.png)

**Figure S26.** Photographs of S-C244. Crystal on the right shows pseudomorphosis (desolvated to the anhydrate).
5.4. 4,4’-Bipyridine propionic acid solvate

Figure S27. Photograph of S-C3_{44}.

5.5. 4,4’-Bipyridine butyric acid solvate

Figure S28. Photographs of S-C4_{44}.

5.6. 4,4’-Bipyridine valeric acid solvate

Figure S29. Photograph of S-C5_{44}.
5.7. 4,4’-Bipyridine caproic acid solvate

Figure S30. Photograph of S-C644.

5.8. 4,4’-Bipyridine caprylic acid solvate

Figure S31. Photograph of S-C844.
6. Crystallographic information

6.1. 2,2′-BIPY formic acid solvate (S-C122)

Table S9. Crystallographic data for S-C122.

| Crystal data                      |                |
|----------------------------------|----------------|
| Chemical formula                 | C₁₀H₈N₂·2(CH₂O₂) |
| \( M_r \)                        | 248.24         |
| Crystal system, space group      | Orthorhombic, Pbc2₁ |
| Temperature (K)                  | 193            |
| \( a, b, c \) (Å)                | 3.7087 (6), 15.9130 (2), 19.8320 (3) |
| \( V \) (Å³)                     | 1170.42 (19)   |
| \( Z \)                          | 4              |
| Radiation type                   | Mo Ka          |
| \( m \) (mm⁻¹)                   | 0.11           |
| Crystal size (mm)                | 0.59 × 0.22 × 0.16 |

| Data collection                   |                |
|----------------------------------|----------------|
| Diffractometer                   | Xcalibur, Ruby, Gemini ultra |
| Absorption correction            | CrysAlis PRO 1.171.40.84a (Rigaku Oxford Diffraction, 2020) |
|                                  | Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. |
| \( T_{\text{min}}, T_{\text{max}} \) | 0.959, 0.987 |
| No. of measured, independent and observed \([I > 2s(I)]\) reflections | 5849, 2462, 1613 |
| \( R_{\text{int}} \)              | 0.066          |
| \( (\sin \theta/\lambda)_{\text{max}} \) (Å⁻¹) | 0.670 |

| Refinement                       |                |
|----------------------------------|----------------|
| \( R(F² > 2s(F²)), wR(F²), S \)  | 0.08, 0.226, 1.06 |
| No. of reflections               | 2462           |
| No. of parameters                | 177            |
| No. of restraints                | 7              |
| H-atom treatment                 | H atoms treated by a mixture of independent and constrained refinement |
| Largest diff. peak and hole (e Å³) | 0.53, -0.42 |
### 6.2. **4,4’-BIPY propionic acid solvate (S-C34)**

**Table S10. Crystallographic data for S-C34.**

| Crystal data |  |
|--------------|---|
| **Chemical formula** | C₆H₆O₂·0.5(C₁₀H₈N₂) |
| **M_r** | 152.17 |
| **Crystal system, space group** | Triclinic, P-1 |
| **Temperature (K)** | 193 |
| **a, b, c (Å)** | 5.2183 (6), 6.2686 (7), 13.0250 (2) |
| **a, b, g (°)** | 96.043 (1), 100.824 (1), 103.952 (1) |
| **V (Å³)** | 401.04 (6) |
| **Z** | 2 |
| **Radiation type** | Mo Kα |
| **m (mm⁻¹)** | 0.09 |
| **Crystal size (mm)** | 0.97 × 0.61 × 0.15 |

| Data collection |  |
|----------------|---|
| **Diffractometer** | Xcalibur, Ruby, Gemini ultra |
| **Absorption correction** | CrysAlis PRO 1.171.40.84a (Rigaku Oxford Diffraction, 2020) |
| Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. |
| **T_min, T_max** | 0.651, 1.000 |
| **No. of measured, independent and observed [I > 2σ(I)] reflections** | 2822, 1846, 1282 |
| **R_int** | 0.020 |
| **(sin θ/λ)_{max} (Å⁻¹)** | 0.701 |

| Refinement |  |
|-------------|---|
| **R[F² > 2σ(F²)], wR(F²), S** | 0.051, 0.147, 1.03 |
| **No. of reflections** | 1846 |
| **No. of parameters** | 126 |
| **No. of restraints** | 37 |
| **H-atom treatment** | H atoms treated by a mixture of independent and constrained refinement |
| **Largest diff. peak and hole (e Å⁻³)** | 0.16, -0.21 |
### 4,4′-BIPY butyric acid solvate (S-C444)

**Table S11.** Crystallographic data for *S-C444*.

| Crystal data                     |                  |
|----------------------------------|------------------|
| Chemical formula                 | C₄H₈O₂·0.5(C₁₀H₈N₂) |
| Mᵣ                               | 166.2            |
| Crystal system, space group      | Triclinic, *P*₁   |
| Temperature (K)                  | 193              |
| a, b, c (Å)                      | 5.230 (3), 6.240 (2), 14.119 (10) |
| a, b, g (°)                      | 87.52 (4), 83.59 (5), 78.10 (4) |
| V (Å³)                           | 448.0 (4)        |
| Z                                | 2                |
| Radiation type                   | Mo Ka            |
| m (mm⁻¹)                         | 0.09             |
| Crystal size (mm)                | 0.76 × 0.28 × 0.11 |

| Data collection                  |                  |
|----------------------------------|------------------|
| Diffractometer                   | Xcalibur, Ruby, Gemini ultra |
| Absorption correction            | CrysAlis PRO 1.171.40.84a (Rigaku Oxford Diffraction, 2020) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. |
| T_min, T_max                     | 0.306, 1.000     |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 2825, 1838, 586 |
| R_int                            | 0.053            |
| (sin θ/λ)max (Å⁻¹)               | 0.676            |

| Refinement                       |                  |
|----------------------------------|------------------|
| R[F² > 2σ(F²)], wR[F²], S        | 0.119, 0.397, 0.98 |
| No. of reflections               | 1838             |
| No. of parameters                | 112              |
| H-atom treatment                 | H-atom parameters constrained |
| Largest diff. peak and hole (e Å⁻³) | 0.34, -0.30     |
6.4. 4,4’-BIPY valeric acid solvate (S-C544)

Table S12. Crystallographic data for S-C544.

| Crystal data                  |                             |
|-------------------------------|-----------------------------|
| Chemical formula              | 0.5(C₁₀H₈N₂)·C₅H₁₀O₂        |
| \( M_r \)                     | 180.22                      |
| Crystal system, space group   | Triclinic, \( P\bar{1} \)   |
| Temperature (K)               | 193                         |
| \( a, b, c \) (Å)             | 5.1355 (11), 6.3797 (12), 15.658 (4) |
| \( \alpha, \beta, \gamma \) (°) | 82.443 (19), 89.93 (2), 80.595 (17) |
| \( V \) (Å³)                  | 501.60 (19)                 |
| \( Z \)                       | 2                           |
| Radiation type                | Mo Kα                       |
| \( m \) (mm⁻¹)                | 0.08                        |
| Crystal size (mm)             | 0.54 × 0.31 × 0.14          |

| Data collection               |                             |
|-------------------------------|-----------------------------|
| Diffractometer                | Xcalibur, Ruby, Gemini ultra|
| Absorption correction        | CrysAlis PRO 1.171.40.84a (Rigaku Oxford Diffraction, 2020) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. |
| \( T_{\text{min}}, T_{\text{max}} \) | 0.637, 1.000               |
| No. of measured,              |                             |
| independent and              |                             |
| observed \([ I > 2s(I) ]\)   | 3024, 2036, 1032            |
| reflections                   |                             |
| \( R_{\text{int}} \)         | 0.040                       |
| \( \langle \sin \theta/\lambda \rangle_{\text{max}} \) (Å⁻¹) | 0.683                      |

| Refinement                    |                             |
|-------------------------------|-----------------------------|
| \( R[F^2 > 2s(F^2)], wR(F^2), S \) | 0.064, 0.168, 1.00          |
| No. of reflections            | 2036                        |
| No. of parameters             | 124                         |
| No. of restraints             | 1                           |
| H-atom treatment             | H atoms treated by a mixture of independent and constrained refinement |
| Largest diff. peak and hole (e Å⁻³) | 0.20, -0.24                |
6.5. 4,4'-BIPY caproic acid solvate (S-C644)

Table S13. Crystallographic data for S-C644.

| Crystal data            |                      |
|-------------------------|----------------------|
| Chemical formula        | C₆H₁₂O₂·0.5(C₁₀H₈N₂) |
| M_r                    | 194.25               |
| Crystal system, space group | Triclinic, P-1       |
| Temperature (K)         | 193                  |
| a, b, c (Å)             | 5.0207 (7), 6.654 (1), 16.974 (2) |
| a, b, g (°)             | 100.654 (12), 93.111 (12), 97.602 (12) |
| V (Å³)                  | 550.58 (13)          |
| Z                       | 2                    |
| Radiation type          | Mo Kα                |
| m (mm⁻¹)                | 0.08                 |
| Crystal size (mm)       | 0.54 × 0.31 × 0.14   |

| Data collection         |                      |
|-------------------------|----------------------|
| Diffractometer          | Xcalibur, Ruby, Gemini ultra |
| Absorption correction   | CrysAlis PRO 1.171.40.84a (Rigaku Oxford Diffraction, 2020) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. |
| Tₘᵡᵣ, Tₘᵃₓ            | 0.619, 1.000         |
| No. of measured, independent and observed [I > 2s(I)] reflections | 3567, 2310, 1309 |
| R_int                   | 0.027                |
| (sin θ/λ)max (Å⁻¹)      | 0.687                |

| Refinement              |                      |
|-------------------------|----------------------|
| R[F² > 2σ(F²)], wR(F²), S | 0.056, 0.155, 0.98   |
| No. of reflections      | 2310                 |
| No. of parameters       | 180                  |
| No. of restraints       | 127                  |
| H-atom treatment        | H atoms treated by a mixture of independent and constrained refinement |
| Largest diff. peak and hole (e Å⁻³) | 0.16, -0.15  |
### 6.6. 4,4′-BIPY caprylic acid solvate (S-C8₄₄)

**Table S14. Crystallographic data for S-C8₄₄.**

| Crystal data                  |
|-------------------------------|
| Chemical formula               | C₁₀H₈N₂·2(C₈H₁₆O₂) |
| $M_r$                         | 444.6              |
| Crystal system, space group   | Triclinic, $P\bar{1}$ |
| Temperature (K)               | 193                |
| $a$, $b$, $c$ (Å)             | 8.9108 (9), 9.6304 (12), 16.4710 (2) |
| $a$, $b$, $g$ (°)             | 98.997 (11), 93.962 (10), 113.384 (11) |
| $V$ (Å³)                      | 1267.9 (2)         |
| $Z$                           | 2                  |
| Radiation type                | Mo Kα              |
| $m$ (mm⁻¹)                    | 0.08               |
| Crystal size (mm)             | 0.98 × 0.23 × 0.11 |

#### Data collection

| Diffractometer                | Xcalibur, Ruby, Gemini ultra |
|-------------------------------|-----------------------------|
| Absorption correction        | CrysAlis PRO 1.171.40.84a (Rigaku Oxford Diffraction, 2020) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. |
| $T_{min}$, $T_{max}$          | 0.955, 1.000                |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 9155, 5833, 3635 |
| $R_{int}$                     | 0.050                        |
| $|\sin \theta|/\lambda$ max (Å⁻¹) | 0.705                        |

#### Refinement

| $R(F^2 > 2σ(F^2))$, $wR(F^2)$, $S$ | 0.054, 0.145, 1.02 |
| No. of reflections               | 5833       |
| No. of parameters                | 300        |
| No. of restraints                | 2          |
| H-atoms treatment               | H atoms treated by a mixture of independent and constrained refinement |
| Largest diff. peak and hole (e Å⁻³) | 0.27, -0.21 |
6.7. 4,4′-BIPY butyric acid solvate (S-C444) – res file

| TITL S-C444 |
|-------------|
| CELL 0.71073 5.23 6.24 14.119 87.52 83.59 78.10 |
| ZERR 2 0.003 0.020 0.001 0.04 0.05 0.04 |
| LATT 1 |
| SFAC 1 0.5 0.5 0.5 |
| UNIT 18 24 2 4 |
| FVAR 1.00 |
| C1  1  0.396900 0.966400 0.534800 1.000000 0.036000 0.040000 |
| N1  3  0.013200 0.840200 0.665800 1.000000 0.060000 0.054000 |
| C2  1  0.286200 0.788300 0.519300 1.000000 0.061000 0.033000 |
| H2  2  0.340542 0.705670 0.462999 1.000000 0.070000 0.040000 |
| C3  1  0.311400 1.075800 0.617300 1.000000 0.061000 0.054000 |
| H3  2  0.384624 1.195955 0.632031 1.000000 0.086000 0.040000 |
| C4  1  0.097700 0.732800 0.586100 1.000000 0.062000 0.049000 |
| H4  2  0.021490 0.610601 0.574277 1.000000 0.081000 0.040000 |
| C5  1  0.116000 1.010300 0.679700 1.000000 0.062000 0.059000 |
| H5  2  0.053166 0.92755 0.735606 1.000000 0.081000 0.040000 |
| O1  4  0.650800 0.461100 0.699600 1.000000 0.103000 0.063000 |
| O2  4  0.662300 0.724800 0.796300 1.000000 0.091000 0.066000 |
| H6’1 2  0.366349 0.579149 0.903746 1.000000 0.125000 |
| H6’2 2  0.200904 0.529478 0.821708 1.000000 0.125000 |
| C8  1  0.425300 0.259800 0.874200 1.000000 0.094000 0.069000 |
| H8’1 2  0.594937 0.222887 0.901995 1.000000 0.114000 |
| H8’2 2  0.442059 0.171228 0.816490 1.000000 0.114000 |
| C9  1  0.212000 0.197500 0.945900 1.000000 0.085000 0.096000 |
| H9’1 2  0.235850 0.240349 1.009748 1.000000 0.144000 |
| H9’2 2  0.223543 0.038809 0.945232 1.000000 0.144000 |
| H9’3 2  0.039266 0.273190 0.928784 1.000000 0.144000 |

END
7. **2,2’-Bipy and 4,4’-Bipy Anhydrates and Hydrate**

7.1. **Powder X-ray diffractometry**

The experimentally measured PXRD patterns are contrasted to the from the single crystal structure simulated PXRD patterns (Figure S32).

![Figure S32](image)

**Figure S32.** Comparison of experimental 2,2’- and 4,4’-Bipy powder patterns (red – anhydrates, blue – hydrate) to the from the single crystal structures simulated PXRD patterns (black).

7.2. **Infrared spectroscopy**

![Figure S33](image)

**Figure S33.** Comparison of 2,2’- and 4,4’-Bipy IR spectra (red – anhydrates, blue – hydrate).
7.3. Gravimetric moisture (de)sorption

The time vs. mass curve (water content) of 2,2'-BIPY shows a continuous mass loss, nearly independent of the relative humidity (Figure S34). The mass loss can be related to sublimation of the compound.

**Figure S34.** Time vs. mass (expressed as water content) curve of the 2,2'-BIPY anhydrate moisture sorption/desorption experiment recorded at 25 °C.
8. Solvates of 2,2’-BIPY and 4,4’-BIPY

8.1. Powder X-ray diffractometry

Figure S35. Comparison of the PXRD pattern of S-C1\textsubscript{22} (green) to the from the single crystal structure simulated PXRD pattern (black).

Figure S36. Comparison of the PXRD patterns of 4,4’-BIPY solvates (green) to the from the single crystal structures simulated PXRD patterns (black).
8.2. **Infrared spectroscopy**

![Figure S37](image)

**Figure S37.** Comparison of the IR spectra of 2,2'-BIPY (green) and 4,4'-BIPY solvates (blue).

8.3. **Hot-stage microscopy**

Figure S38 shows exemplarily a contact preparation (melt film) of S-C$_{24}$ and AH$_{24}$. The “black line” at the contact zone of the two compounds relates to the eutectic temperature and forms at approx. 70 °C.

![Figure S38](image)

**Figure S38.** Contact preparation of S-C$_{24}$ and AH$_{24}$ showing the eutectic temperature at 70 °C (encircled).
9. Stability at ambient conditions

All solvates were subjected to storage stability experiments at ambient conditions (RT, 30 – 40% RH), and transformations monitored with PXRD. The diffractograms were recorded at first hourly and then daily. Only a selection of the recorded diffractograms is given.

**Figure S39.** PXRD measurements monitoring the desolvation process of S-C1a at ambient conditions (t = x hours). Reference patterns are provided for the anhydrate (AH), hydrate (Hy2) and the solvate (SC and PBE-TS – simulated from the single crystal structure and optimized solvate structure, respectively).
Figure S40. PXRD measurements monitoring the desolvation process of S-C2 at ambient conditions (t = x hours). Reference patterns are provided for the anhydrate (AH), hydrate (Hy2) and the solvate (SC and PBE-TS – simulated from the single crystal structure and optimized solvate structure, respectively).

Figure S41. PXRD measurements monitoring the desolvation process of S-C3 at ambient conditions (t = x hours). Reference patterns are provided for the anhydrate (AH), hydrate (Hy2) and the solvate (SC and PBE-TS – simulated from the single crystal structure and optimized solvate structure, respectively).
**Figure S42.** PXRD measurements monitoring the desolvation process of S-C4₄₄ at ambient conditions (t = x hours). Reference patterns are provided for the anhydrate (AH), hydrate (Hy2) and the solvate (SC and PBE-TS – simulated from the single crystal structure and optimized solvate structure, respectively).

**Figure S43.** PXRD measurements monitoring the desolvation process of S-C5₄₄ at ambient conditions (t = x hours). Reference patterns are provided for the anhydrate (AH), hydrate (Hy2) and the solvate (SC and PBE-TS – simulated from the single crystal structure and optimized solvate structure, respectively).
Figure S44. PXRD measurements monitoring the desolvation process of S-C6 and S-C8 at ambient conditions (t = x hours). Reference patterns are provided for the anhydrate (AH), hydrate (Hy2) and the solvate (SC – simulated from the single crystal structures).
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