**Supporting Information**

# Guest-Adaptive Hydrogen-Bonded Dimerization of a *C*$_3$-Symmetric Tribenzotriquinacene Molecular Bowl

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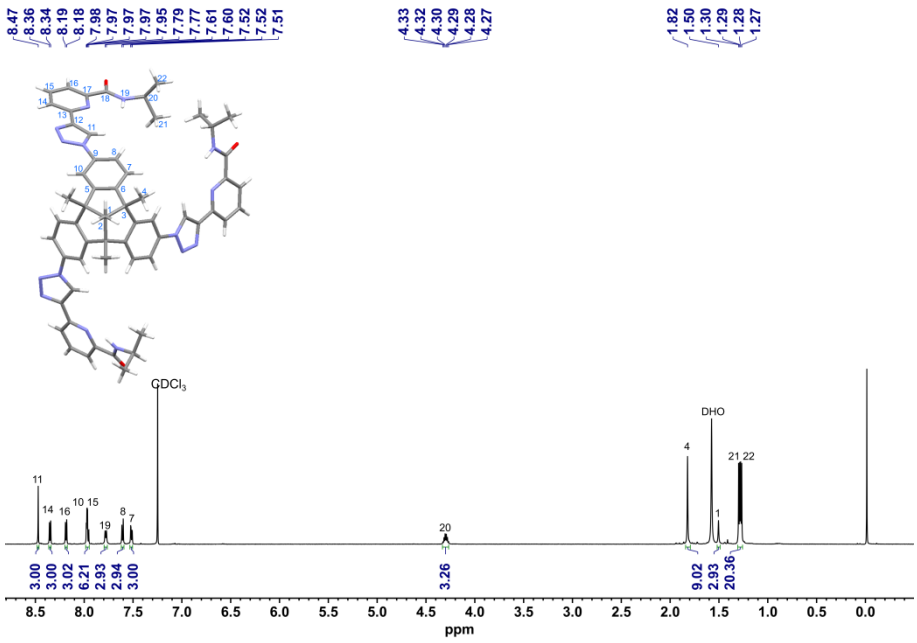


Figure S1. $^{1}$H NMR spectrum of $C_3$-**1** (400 MHz, 298 K, $CDCl_3$).

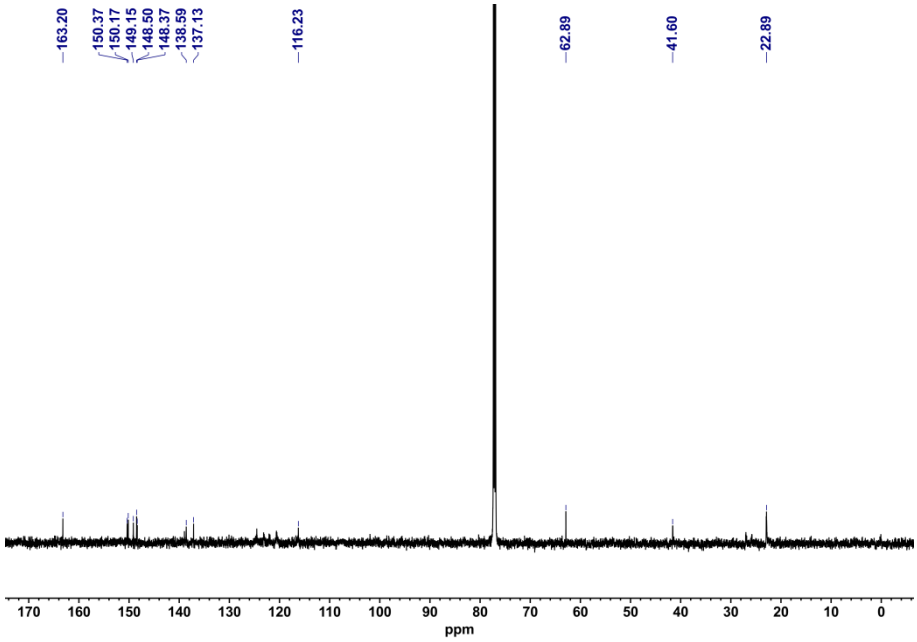


Fig. S2. $^{13}$C NMR spectrum of $C_3$-**1** (101 MHz, 298 K, $CDCl_3$).

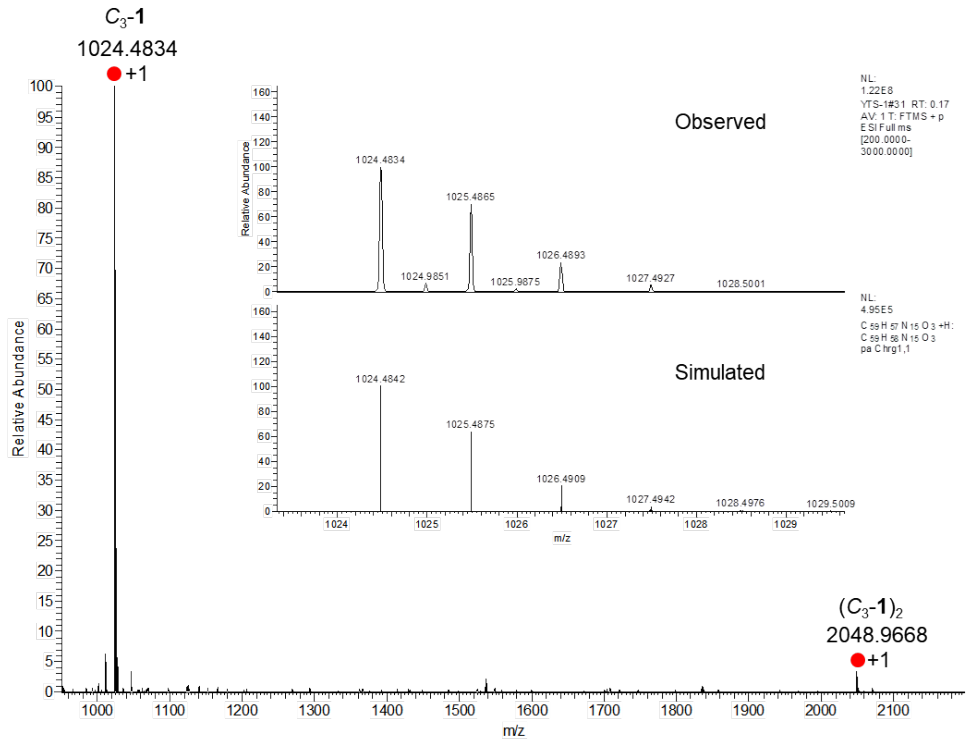


Fig. S3. MS of $C_3$-**1** with the comparison of observed and simulated isotopic patterns of the peaks +1.

## 2. Analysis of Host-Guest Interaction

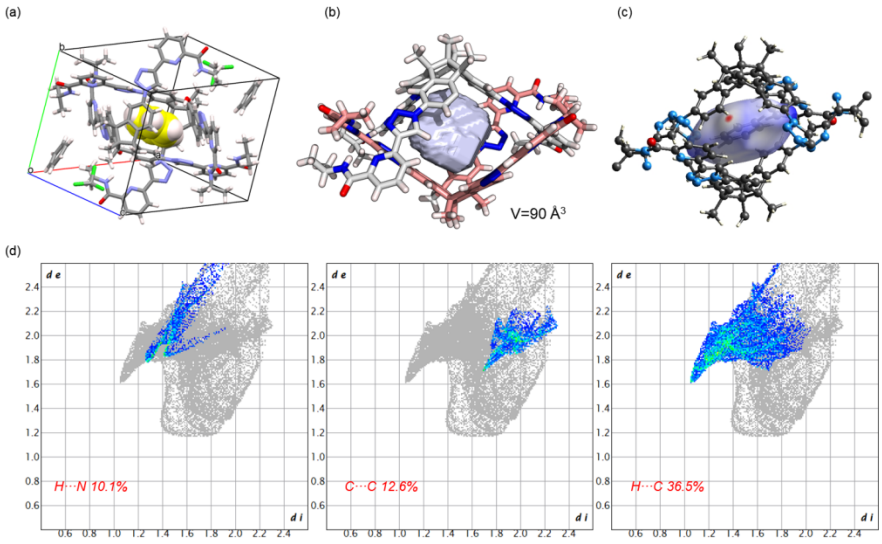


Fig. S4. (a) Crystal structures of the host-guest complexes Ph⊂($C_3$-**1**)$_2$.[2] (b) Cavity volume calculation diagram of host framework in Ph⊂($C_3$-**1**)$_2$ (guest molecule was omitted).[3] (c) Hirshfeld surface of Ph⊂($C_3$-**1**)$_2$ mapped with $d_{norm}$, highlighting the

close intermolecular contacts near the guest Ph (Colour scheme: red for shorter contacts, white for contacts around the vdw separation, and blue for longer contacts).[4] (d) 2D fingerprint plots for Ph⊂($C_3$-**1**)$_2$, resolved into H···N (left), C···C (middle), and H···C (right) contacts. [4]

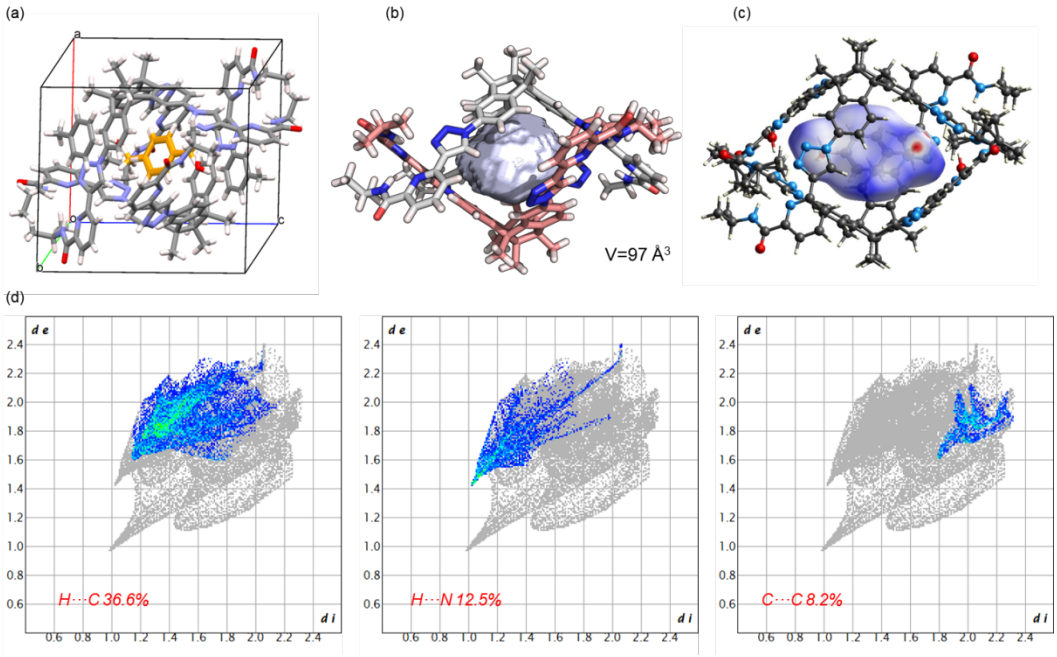


Fig. S5. (a) Crystal structures of the host-guest complexes for PhMe⊂($C_3$-**1**)$_2$. (b) Cavity volume calculation diagram of host framework in PhMe⊂($C_3$-**1**)$_2$ (guest molecule was omitted) (c) Hirshfeld surface of PhMe⊂($C_3$-**1**)$_2$ mapped with $d_{norm}$ showing the close intermolecular contacts near the guest PhMe (Colour scheme: red for shorter contacts, white for contacts around the vdw separation, and for longer contacts). (d) 2D fingerprint plots for PhMe⊂($C_3$-**1**)$_2$, resolved into H···C (left), H···N (middle), and C···C (right) contacts.

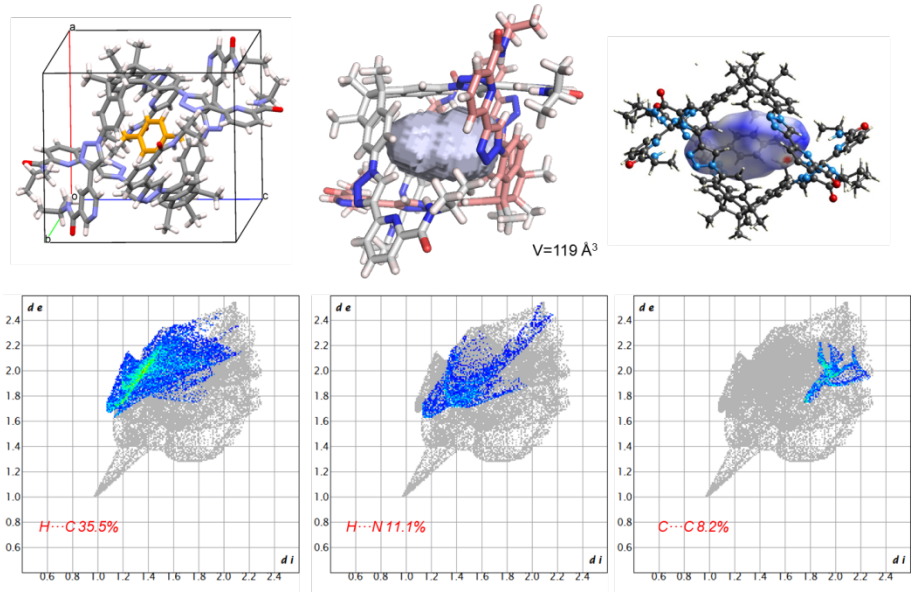


Fig. S6. (a) Crystal structures of host-guest complexes for *p*-xylene⊂($C_3$-**1**)$_2$. (b) Cavity volume calculation diagram of host framework in *p*-xylene⊂($C_3$-**1**)$_2$ (guest molecule was omitted) (c) Hirshfeld surface of *p*-xylene⊂($C_3$-**1**)$_2$ mapped with $d_{norm}$ showing the close intermolecular contacts near the guest *p*-xylene (Colour scheme: red for shorter contacts, white for contacts around the vdw separation, and blue for longer contacts). (d) 2D fingerprint plots for *p*-xylene⊂($C_3$-**1**)$_2$, resolved into H···C (left), H···N (middle), and C···C (right) contacts.

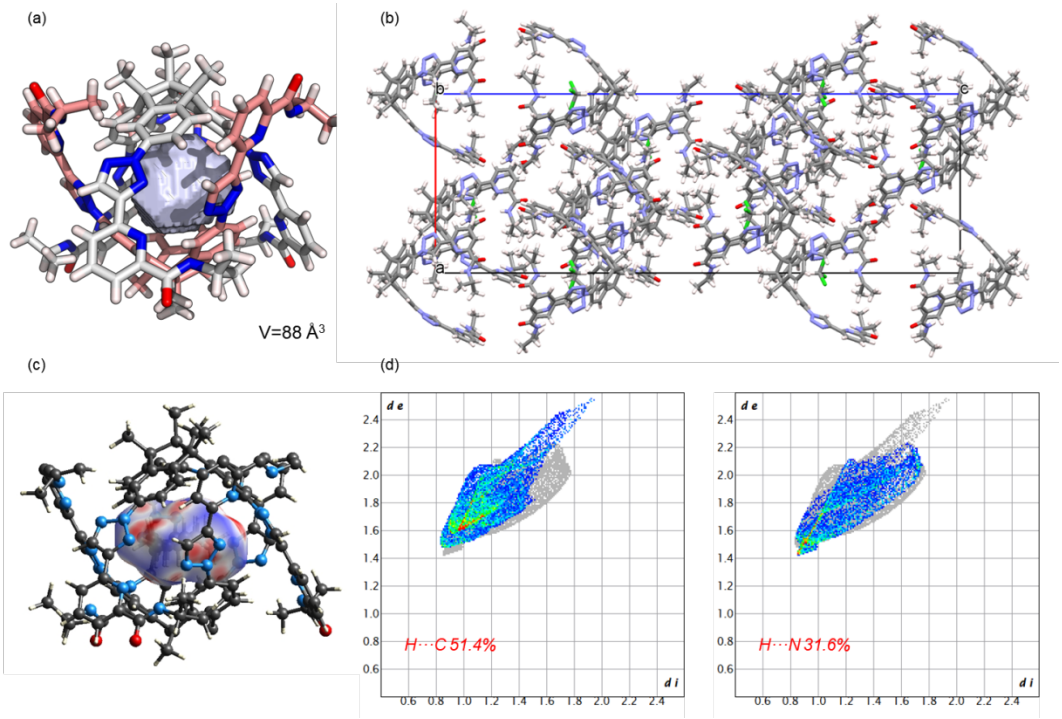


Fig. S7. (a) Cavity volume calculation diagram of host framework of CYH⊂($C_3$-**1**)$_2$ (guest molecule was omitted). (b) Crystal structures of host-guest complexes for CYH⊂($C_3$-**1**)$_2$. (c) Hirshfeld surface of CYH⊂($C_3$-**1**)$_2$ mapped with $d_{norm}$ showing the close intermolecular contacts near the guest CYH (Colour scheme: red for shorter contacts, white for contacts around the vdw separation, and blue for longer contacts). (d) 2D fingerprint plots for CYH⊂($C_3$-**1**)$_2$, resolved into H···C (left), H···N (right) contacts.

## 3. Supplemental figures and tables for crystal data

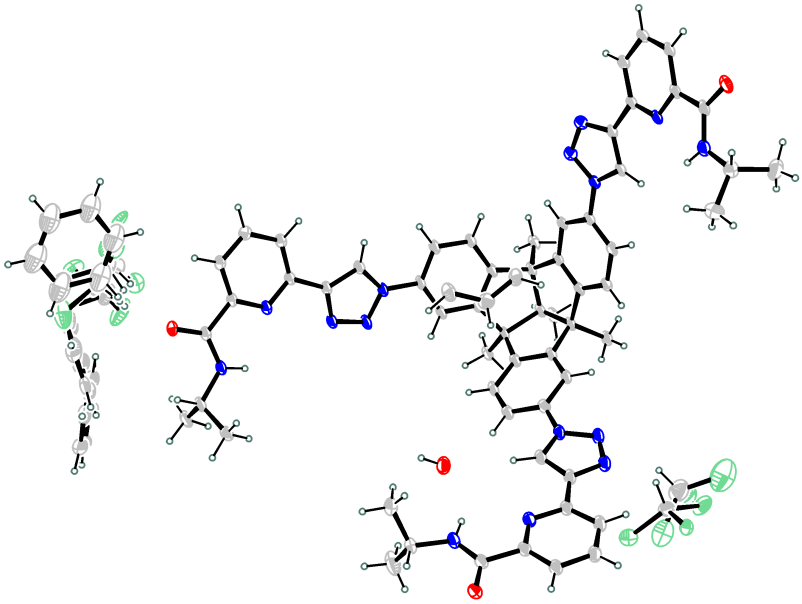

Fig. S8. Ortep-drawing of the asymmetric unit in the crystal structure of Ph⊂($C_3$-**1**)$_2$ at 30% probability level.

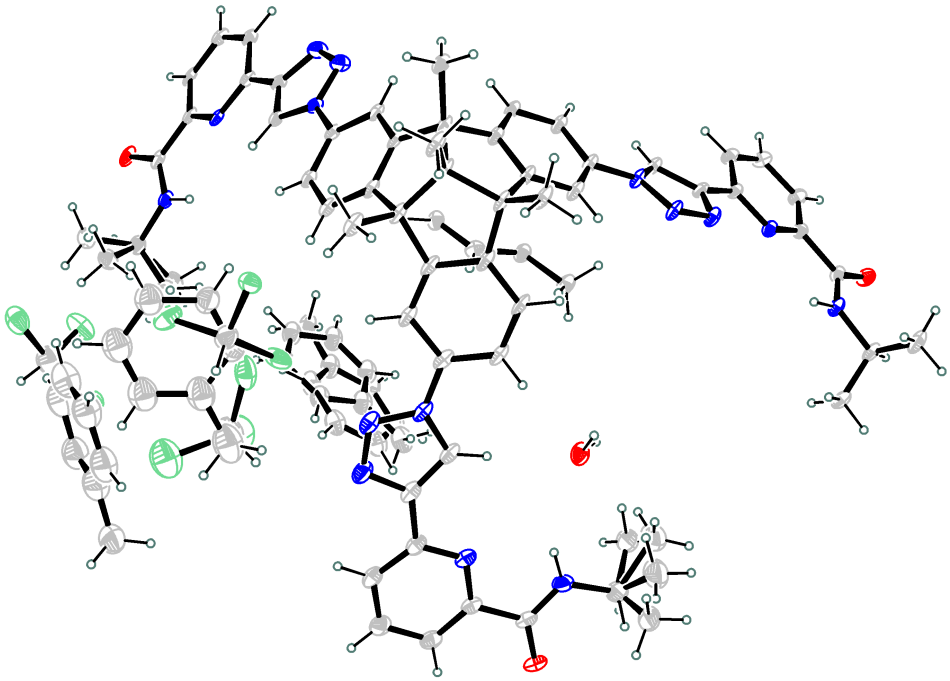

Fig. S9. Ortep-drawing of the asymmetric unit in the crystal structure of PhMe⊂($C_3$-**1**)$_2$ at 30% probability level.

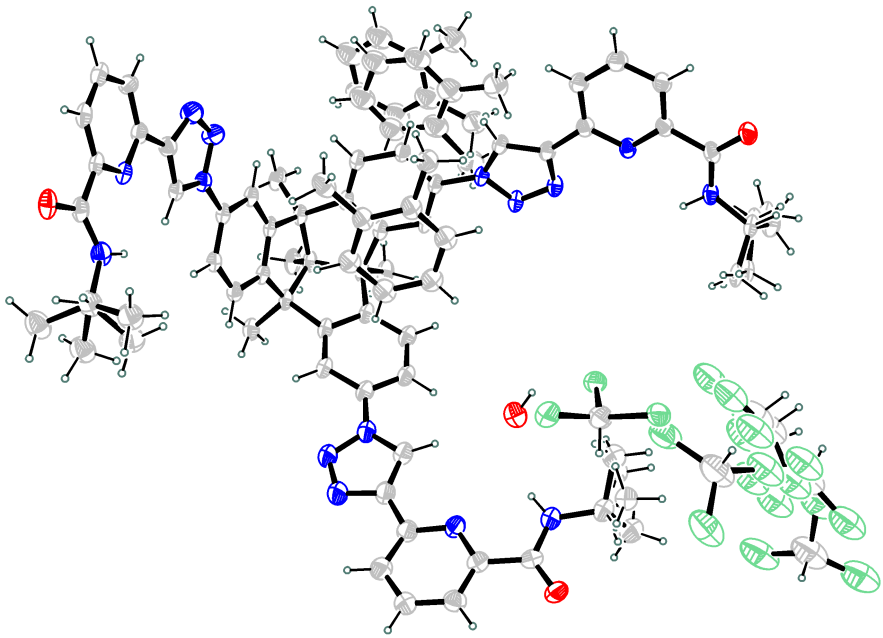

Fig. S10. Ortep-drawing of the asymmetric unit in the crystal structure of *o*-xylene⊂($C_3$-**1**)$_2$ at 30% probability level.

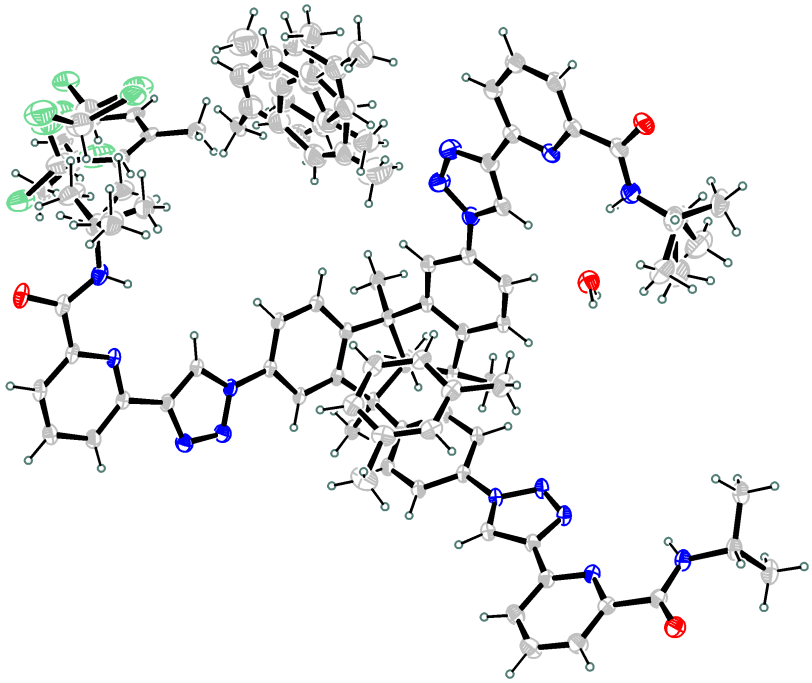

Fig. S11. Ortep-drawing of the asymmetric unit in the crystal structure of *m*-xylene⊂($C_3$-**1**)$_2$ at 30% probability level.

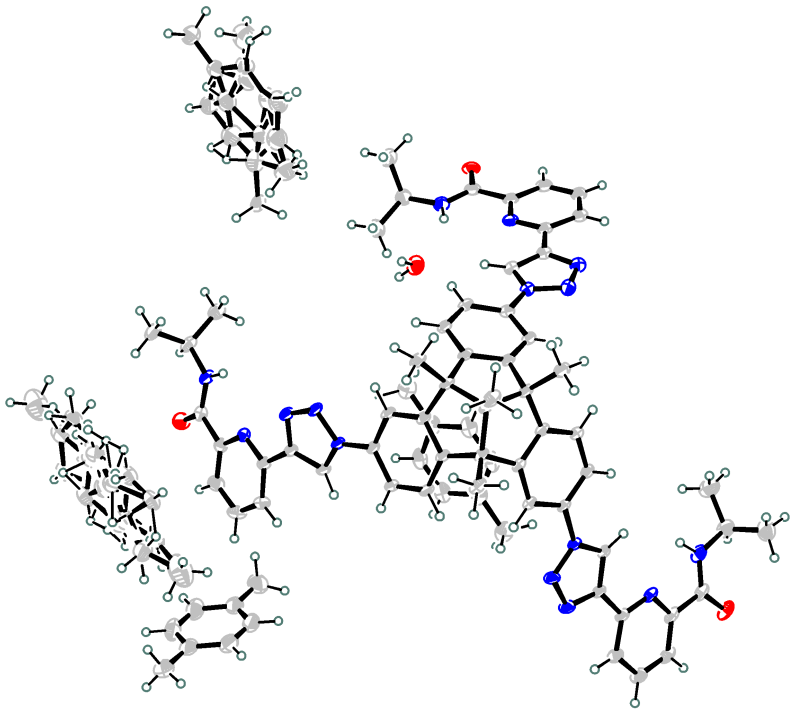

Fig. S12. Ortep-drawing of the asymmetric unit in the crystal structure of *p*-xylene⊂($C_3$-**1**)$_2$ at 30% probability level.

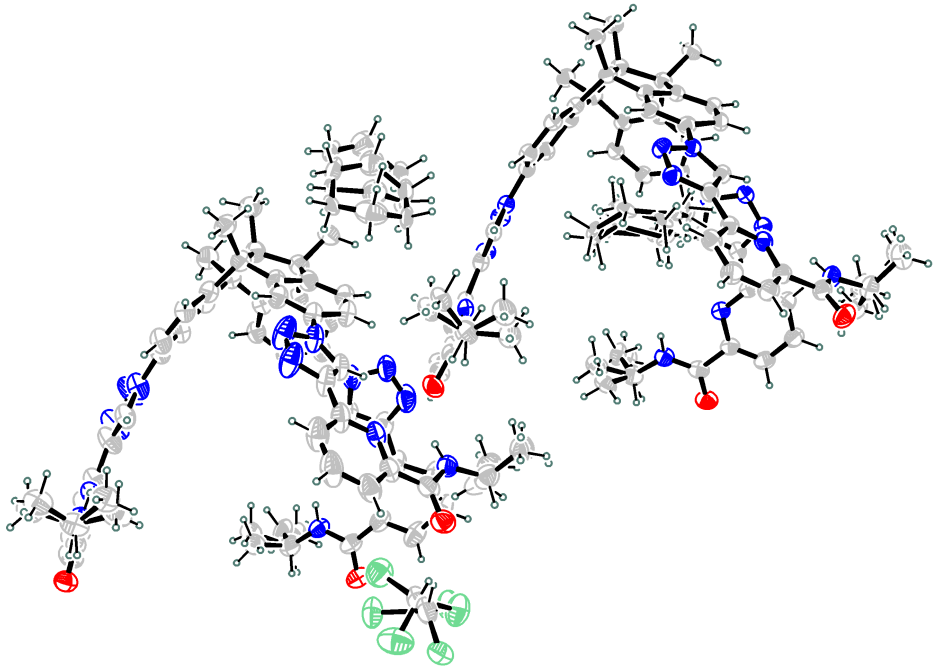

Fig. S13. Ortep-drawing of the asymmetric unit in the crystal structure of CYH⊂($C_3$-**1**)$_2$ at 30% probability level.

Table S1. Crystal data and structure refinement for Ph⊂($C_3$-**1**)$_2$.

| | | |
|---|---|---|
| Identification code | Ph | |
| Empirical formula | $C_{70.20}$ $H_{68.20}$ $Cl_{6.60}$ $N_{15}$ $O_4$ | |
| Formula weight | 1419.96 | |
| Temperature | 100.15 K | |
| Wavelength | 1.3405 Å | |
| Crystal system | Triclinic | |
| Space group | *P*-1 | |
| Unit cell dimensions | a = 14.2295(3) Å | α= 70.136(2)°. |
| | b = 15.4768(3) Å | β= 79.294(2)°. |
| | c = 17.3417(4) Å | γ = 85.330(2)°. |
| Volume | 3528.67(14) Å$^3$ | |
| Z | 2 | |
| Density (calculated) | 1.336 Mg/m$^3$ | |
| Absorption coefficient | 1.924 mm$^{-1}$ | |
| F(000) | 1477 | |
| Crystal size | 0.8 × 0.7 × 0.6 mm$^3$ | |
| Theta range for data collection | 2.389 to 56.017°. | |
| Index ranges | -17<=h<=16, -19<=k<=16, -21<=l<=21 | |
| Reflections collected | 46596 | |
| Independent reflections | 13676 [R(int) = 0.0366] | |
| Completeness to theta = 53.543° | 99.9 % | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 13676 / 1 / 838 | |
| Goodness-of-fit on $F^2$ | 1.068 | |
| Final R indices [I>2sigma(I)] | $R_1$ = 0.0881, $wR_2$ = 0.2705 | |
| R indices (all data) | $R_1$ = 0.1149, $wR_2$ = 0.2954 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 1.060 and -0.800 e.Å$^{-3}$ | |

Table S2. Crystal data and structure refinement for PhMe⊂($C_3$-**1**)$_2$.

| | | |
|---|---|---|
| Identification code | PhMe | |
| Empirical formula | $C_{155}$ $H_{160}$ $Cl_6$ $N_{30}$ $O_8$ | |
| Formula weight | 2783.82 | |
| Temperature | 100.00(10) K | |
| Wavelength | 1.3405 Å | |
| Crystal system | Triclinic | |
| Space group | *P*-1 | |
| Unit cell dimensions | a = 14.3812(3) Å | α= 71.658(2)°. |
| | b = 15.4937(3) Å | β= 79.5378(19)°. |
| | c = 17.2333(4) Å | γ = 82.7903(17)°. |
| Volume | 3574.59(15) Å$^3$ | |
| Z | 1 | |
| Density (calculated) | 1.293 Mg/m$^3$ | |
| Absorption coefficient | 1.087 mm$^{-1}$ | |
| F(000) | 1466 | |
| Crystal size | 0.13 × 0.12 × 0.1 mm$^3$ | |
| Theta range for data collection | 2.376 to 55.126°. | |
| Index ranges | -16<=h<=17, -18<=k<=18, -21<=l<=21 | |
| Reflections collected | 40828 | |
| Independent reflections | 13351 [R(int) = 0.0736] | |
| Completeness to theta = 53.543° | 99.5 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 1.00000 and 0.80499 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 13351 / 790 / 1165 | |
| Goodness-of-fit on F$^2$ | 1.096 | |
| Final R indices [I>2sigma(I)] | $R_1$ = 0.1378, w$R_2$ = 0.3414 | |
| R indices (all data) | $R_1$ = 0.1928, w$R_2$ = 0.3586 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 1.200 and -0.772 e.Å$^{-3}$ | |

Table S3. Crystal data and structure refinement for *o*-xylene⊂($C_3$-**1**)$_2$.

| | | |
|---|---|---|
| Identification code | o-xylene | |
| Empirical formula | $C_{145}H_{151}Cl_9N_{30}O_8$ | |
| Formula weight | 2761.00 | |
| Temperature | 100.00(10) K | |
| Wavelength | 1.54184 Å | |
| Crystal system | Triclinic | |
| Space group | *P*-1 | |
| Unit cell dimensions | a = 14.8347(8) Å | α= 72.925(5)°. |
| | b = 15.5615(9) Å | β= 81.228(4)°. |
| | c = 16.9145(9) Å | γ = 82.651(4)°. |
| Volume | 3674.6(4) Å$^3$ | |
| Z | 1 | |
| Density (calculated) | 1.248 Mg/m$^3$ | |
| Absorption coefficient | 2.093 mm$^{-1}$ | |
| F(000) | 1448 | |
| Crystal size | 0.13 x 0.12 x 0.1 mm$^3$ | |
| Theta range for data collection | 2.753 to 72.465°. | |
| Index ranges | -17<=h<=18, -19<=k<=19, -20<=l<=20 | |
| Reflections collected | 40218 | |
| Independent reflections | 14035 [R(int) = 0.1406] | |
| Completeness to theta = 67.684° | 99.5 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 1.00000 and 0.82976 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 14035 / 1488 / 1276 | |
| Goodness-of-fit on F$^2$ | 1.167 | |
| Final R indices [I>2sigma(I)] | $R_1$ = 0.1353, $wR_2$ = 0.3432 | |
| R indices (all data) | $R_1$ = 0.2876, $wR_2$ = 0.4357 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.569 and -0.471 e.Å$^{-3}$ | |

Table S4. Crystal data and structure refinement for *m*-xylene⊂($C_3$-**1**)$_2$.

| | | |
|---|---|---|
| Identification code | m-xylene | |
| Empirical formula | $C_{150.98}$ $H_{158.98}$ $Cl_3$ $N_{30}$ $O_8$ | |
| Formula weight | 2628.42 | |
| Temperature | 100.00(10) K | |
| Wavelength | 1.54184 Å | |
| Crystal system | Triclinic | |
| Space group | *P*-1 | |
| Unit cell dimensions | a = 14.7305(5) Å | α= 72.734(3)°. |
| | b = 15.2894(5) Å | β= 80.346(3)°. |
| | c = 17.0209(5) Å | γ = 79.345(3)°. |
| Volume | 3571.5(2) Å$^3$ | |
| Z | 1 | |
| Density (calculated) | 1.222 Mg/m$^3$ | |
| Absorption coefficient | 1.121 mm$^{-1}$ | |
| F(000) | 1390 | |
| Crystal size | 0.19 × 0.151 × 0.15 mm$^3$ | |
| Theta range for data collection | 2.738 to 78.556°. | |
| Index ranges | -18<=h<=18, -19<=k<=17, -20<=l<=20 | |
| Reflections collected | 47371 | |
| Independent reflections | 14050 [R(int) = 0.0724] | |
| Completeness to theta = 67.684° | 99.5 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 1.00000 and 0.87605 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 14050 / 1065 / 1252 | |
| Goodness-of-fit on F$^2$ | 1.026 | |
| Final R indices [I>2sigma(I)] | $R_1$ = 0.0850, $wR_2$ = 0.2310 | |
| R indices (all data) | $R_1$ = 0.1191, $wR_2$ = 0.2611 | |
| Extinction coefficient | 0.0035(5) | |
| Largest diff. peak and hole | 0.588 and -0.473 e.Å$^{-3}$ | |

Table S5. Crystal data and structure refinement for *p*-xylene⊂($C_3$-**1**)$_2$.

| | | |
|---|---|---|
| Identification code | p-xylene | |
| Empirical formula | $C_{83}$ $H_{89}$ $N_{15}$ $O_4$ | |
| Formula weight | 1360.69 | |
| Temperature | 100.00(10) K | |
| Wavelength | 1.54184 Å | |
| Crystal system | Triclinic | |
| Space group | *P*-1 | |
| Unit cell dimensions | a = 14.6409(5) Å | α= 71.798(3)°. |
| | b = 15.4829(5) Å | β= 80.271(3)°. |
| | c = 17.0956(5) Å | γ = 79.849(3)°. |
| Volume | 3596.8(2) Å$^3$ | |
| Z | 2 | |
| Density (calculated) | 1.256 Mg/m$^3$ | |
| Absorption coefficient | 0.630 mm$^{-1}$ | |
| F(000) | 1448 | |
| Crystal size | 0.4 × 0.3 × 0.2 mm$^3$ | |
| Theta range for data collection | 2.741 to 77.085°. | |
| Index ranges | -17<=h<=18, -16<=k<=19, -20<=l<=21 | |
| Reflections collected | 48157 | |
| Independent reflections | 14306 [R(int) = 0.0867] | |
| Completeness to theta = 67.684° | 99.5 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 1.00000 and 0.58764 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 14306 / 593 / 1128 | |
| Goodness-of-fit on F$^2$ | 1.028 | |
| Final R indices [I>2sigma(I)] | $R_1$ = 0.0739, w$R_2$ = 0.1878 | |
| R indices (all data) | $R_1$ = 0.0914, w$R_2$ = 0.1980 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.725 and -0.516 e.Å$^{-3}$ | |

Table S6. Crystal data and structure refinement for CYH⊂($C_3$-**1**)$_2$.

| | | |
|---|---|---|
| Identification code | CYH | |
| Empirical formula | $C_{146.20}$ $H_{163.20}$ $Cl_{21.60}$ $N_{30}$ $O_6$ | |
| Formula weight | 3202.38 | |
| Temperature | 100.02(10) K | |
| Wavelength | 1.54184 Å | |
| Crystal system | Trigonal | |
| Space group | *R*-3 | |
| Unit cell dimensions | a = 22.8874(11) Å | α= 90°. |
| | b = 22.8874(11) Å | β= 90°. |
| | c = 57.200(5) Å | γ = 120°. |
| Volume | 25949(3) Å$^3$ | |
| Z | 6 | |
| Density (calculated) | 1.230 Mg/m$^3$ | |
| Absorption coefficient | 3.585 mm$^{-1}$ | |
| F(000) | 9994 | |
| Crystal size | 0.13 x 0.12 x 0.1 mm$^3$ | |
| Theta range for data collection | 2.359 to 66.564°. | |
| Index ranges | -15<=h<=27, -27<=k<=19, -63<=l<=67 | |
| Reflections collected | 29664 | |
| Independent reflections | 9828 [R(int) = 0.0465] | |
| Completeness to theta = 66.564° | 96.2 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 1.00000 and 0.56595 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 9828 / 390 / 711 | |
| Goodness-of-fit on F$^2$ | 1.456 | |
| Final R indices [I>2sigma(I)] | $R_1$ = 0.1446, $wR_2$ = 0.3752 | |
| R indices (all data) | $R_1$ = 0.1723, $wR_2$ = 0.4041 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.816 and -0.409 e.Å$^{-3}$ | |

**REFERENCES**


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