**Supporting Information**

for

# Coordination Chemistry of Polynitriles, Part XI. Influence of 4,4′-Bipyridine and Solvent on the Crystal and Molecular Structures of Alkaline Earth Pentacyanocyclopentadienides

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# 1. TABLES

*Table S 1: Hydrogen bond parameters of O–H donors*

| *Compound* | *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* | *Symm. Oper.* |
|---|---|---|---|---|---|---|
| **1** | O1-H1A…O3 | 0.86(4) | 1.72(4) | 2.583(3) | 176(3) | *x, y, z* |
| | O1-H1B…N104 | 0.89(4) | 2.01(4) | 2.885(3) | 168(3) | *x, y, z* |
| | O2-H2A…N103 | 0.79(4) | 2.16(4) | 2.934(3) | 167(3) | *-x, y, 2.5-z* |
| | O2-H2B…N101 | 0.86/5) | 2.07(5) | 2.894(3) | 162 | *½ +x, y- ½, z* |
| | O3-H3…N11 | 0.84(5) | 1.90(5) | 2.728(3) | 169 | *x- ½, ½ -y, 2-z* |
| **2** | O1-H1W…N103 | 0.87(2) | 2.04(2) | 2.889(5) | 166(4) | *1-x, ½ +y, 1-z* |
| | O1-H2W…N2 | 0.87(2) | 1.91(3) | 2.733(5) | 158(4) | *1-x, y- ½, -z* |
| | O2-H3W…N5 | 0.89(2) | 1.84(3) | 2.712(5) | 166(4) | *1+x, y, z-1* |
| | O2-H4W…N101 | 0.87(2) | 2.10(3) | 2.885(5) | 151(4) | *x, y, z-1* |
| | O3-H5W…N4 | 0.87(2) | 1.87(2) | 2.725(5) | 169(5) | *2-x, ½ +y, 1-z* |
| | O3-H6W…N205 | 0.87(2) | 2.08(3) | 2.906(5) | 158(4) | *1+x, y, z* |
| | O4-H7W…N203 | 0.89(2) | 2.04(3) | 2.893(5) | 161(4) | *1-x, ½ +y, 1-z* |
| | O4-H8W…N6 | 0.90(2) | 1.83(2) | 2.726(4) | 169(4) | *x, y, z* |
| **3** | O11-H11M…N10 | 0.84 | 1.95 | 2.769(3) | 166.2 | *1-x, 1-y, 1-z* |
| | O12-H12M…N101 | 0.84 | 2.18 | 2.942(3) | 150.4 | *1+x, ½ -y, ½ +z* |
| | O13-H13M…N9 | 0.84 | 1.95 | 2.772(3) | 166.6 | *-x, 1-y, 1-z* |
| | O14-H14M…N404 | 0.84 | 2.18 | 2.904(3) | 144.8 | *X, ½ -y, ½ +z* |
| | O15-H15M…N5 | 0.84 | 2.03 | 2.817(3) | 155 | *-x, 1-y, 1-z* |
| | O16-H16M…N6 | 0.84 | 1.99 | 2.805(3) | 165 | *1-x, 1-y, 1-z* |
| | O17-H17M…N11 | 0.84 | 2.01 | 2.823(3) | 164 | *-x, 1-y, 1-z* |
| | O18-H18M…N12 | 0.84 | 2.05 | 2.841(3) | 156 | *1-x, 1-y, 1-z* |
| | O21-H21M…N202 | 0.84 | 2.13 | 2.898(3) | 152 | *-x, 1-y, 1-z* |
| | O22-H22M…N2 | 0.84 | 1.94 | 2.771(3) | 170 | *1-x, 1-y, 1-z* |
| | O23-H23M…N1 | 0.84 | 1.97 | 2.794(3) | 166 | *-x, 1-y, 1-z* |
| | O24-H24M…N102 | 0.84 | 2.16 | 2.952(3) | 157 | *-x, ½ +y, ½ -z* |
| | O25-H25M…N7 | 0.84 | 2.02 | 2.827(3) | 162 | *-x, y- ½, ½ -z* |
| | O26-H26M…N8 | 0.84 | 2.02 | 2.843(3) | 165 | *1-x, y- ½ , ½ -z* |
| | O27-H27M…N3 | 0.84 | 1.91 | 2.738(3) | 170 | *-x, 1-y, 1-z* |
| | O28-H28M…N4 | 0.84 | 1.97 | 2.782(3) | 162 | *1-x, 1-y, 1-z* |
| **4** | O1W-H11W…N11 | 0.83(2) | 1.91(2) | 2.724(3) | 169(3) | *-x, 1-y, 1-z* |
| | O1W-H12W…N204 | 0.81(2) | 2.08(2) | 2.874(3) | 163(3) | *-x, -y, -z* |
| | O2W-H21W…N20 | 0.82(2) | 1.98(2) | 2.780(3) | 166(3) | *1-x, -y, 1-z* |
| | O2W-H22W…O1W | 0.82(2) | 2.20(2) | 2.971(2) | 158(3) | *-x,-y, 1-z* |
| | O1B-H1B…N10 | 0.78(3) | 1.95(3) | 2.730(3) | 176(4) | *x-1, y, z* |
| | O2B-H2B…N21 | 0.85(4) | 1.93(4) | 2.770(3) | 170(3) | *x, y, z-1* |

| | | | | | | |
|---|---|---|---|---|---|---|
| | O3B-H3B…N105 | 0.84 | 2.40 | 3.13(2) | 146 | *x, y, 1+z* |
| *Compound* | *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* | *Symm. Oper.* |
| **5** | O13-H13E…N30 | 0.85 | 2.09 | 2.91 | 166 | *1+x, 1-y, z- ½* |
| | O16-H16E…N44 | 0.84 | 2.09 | 2.91 | 166 | |
| | O19-H19E…N103 | 0.85 | 2.08 | 2.88 | 158 | |
| | O22-H22E…O40 | 0.87 | 2.20 | 2.76 | 123 | |
| | O25-H25E…N105 | 0.89 | 2.17 | 2.85 | 133 | |
| | O28-H28E…N104 | 0.83 | 2.02 | 2.84 | 172 | |
| | O31-H31E…N60 | 0.85 | 2.11 | 2.91 | 158 | |
| | O34-H34E…N106 | 0.88 | 2.07 | 2.88 | 154 | |
| | O37-H37E…O43 | 0.86 | 1.94 | 2.72 | 149 | *x-1, y, z* |
| | O40-H40E…N11 | 0.87 | 2.48 | 2.98 | 118 | |
| | O43-H43E…N34 | 0.84 | 2.35 | 3.11 | 152 | *1+x, y, z* |
| | O1W-H11W…O5W | 0.86 | 1.99 | 2.71 | 140 | |
| | O1W-H12W…N1 | 0.86 | 2.57 | 3.25 | 138 | |
| | O2W-H21W…O5W | 0.86 | 2.13 | 2.68 | 121 | |
| | O3W-H31W…N22 | 0.84 | 2.13 | 2.96 | 170 | *x, 1-y, z+ ½* |
| | O3W-H32W…N41 | 0.84 | 2.10 | 2.89 | 158 | *x, 1-y, z- ½* |
| | O4W-H41W…N62 | 0.85 | 2.08 | 2.92 | 171 | *x 1-y, z+ ½* |
| | O4W-H42W…N51 | 0.85 | 2.10 | 2.94 | 172 | *x, 1-y, z- ½* |
| | O5W-H51W…N5 | 0.86 | 1.90 | 2.74 | 166 | *x, 1-y, z- ½* |
| | O5W-H52W…N102 | 0.86 | 1.96 | 2.75 | 152 | *x, 1-y, z+ ½* |
| **6** | O1BU-H1BU…N94 | 0.85 | 2.00 | 2.83 | 165 | *½ -x, y- ½ , 1.5-z* |
| | O5-H5…N9 | 0.85 | 1.92 | 2.77 | 171 | |
| | O6-H6a/b…N4 | 0.84 | 1.93 | 2.77 | 172 | *1.5-x, y- ½ , 1.5-z* |
| | O1W-H11W…N73 | 0.85 | 2.66 | 3.47 | 162 | *1-x, -y, 2-z* |
| | O1W-H12W…N8 | 0.85 | 1.93 | 2.75 | 162 | *1+x, y, z* |
| | O2W-H21W…N91 | 0.85 | 2.05 | 2.90 | 172 | |
| | O2W-H22W…N2 | 0.85 | 1.95 | 2.77 | 162 | *x-1, y, z* |
| | O3W-H31W…O1W | 0.84 | 2.14 | 2.94 | 160 | |
| | O3W-H32W…N7 | 0.84 | 1.93 | 2.75 | 166 | |
| | O4W-H41W…N73 | 0.83 | 2.06 | 2.89 | 175 | *1-x, -y, 2-z* |
| | O4W-H42W…N6 | 0.92 | 1.81 | 2.71 | 165 | *X+1, y, z* |

*Table S 2: Hydrogen bond parameters of the C–H donors*

| *Compound* | *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* | *Symm. Oper.* |
|---|---|---|---|---|---|---|
| **1** | C10-H10…O1 | 0.95 | 2.67 | 3.161(3) | 113 | *-x+ ½ - y + ½, 2-z* |
| | C13-H13…N105 | 0.95 | 2.60 | 3.491(4) | 157 | *x, y, z* |
| | C16-H16…N102 | 0.95 | 2.45 | 3.351(4) | 157 | *1+x, 1-y, z- ½* |
| | C18-H18…N105 | 0.95 | 2.59 | 3.527(4) | 167 | *x, y, z* |
| **2** | C2-H2…N204 | 0.95 | 2.53 | 3,460(7) | 166 | *1-x, ½ +y, 1-z* |
| | C6-H6…N105 | 0.95 | 2.45 | 3.352(7) | 159 | *1-x, ½ +y, -z* |
| | C7-H7…N104 | 0.95 | 2.60 | 3.497(7) | 157 | *1-x, ½ +y, -z* |
| | C9-H9…N204 | 0.95 | 2.58 | 3.500(7) | 162 | *1-x, ½ +y, 1-z* |
| | C11-H11…N101 | 0.95 | 2.69 | 3.633(7) | 172 | *x, y, z-1* |
| | C12-H12…N102 | 0.95 | 2.57 | 3.507(7) | 168 | *x, y, z-1* |
| | C16-H16…N202 | 0.95 | 2.42 | 3.301(7) | 154 | *x+1, y, z+1* |
| | C17-H17…N201 | 0.95 | 2.66 | 3.557(7) | 157 | *x+1, y, z+1* |
| | C19-H19…N102 | 0.95 | 2.62 | 3.549(7) | 166 | *x, y, z-1* |
| **3** | C7-H7…N402 | 0.95 | 2.42 | 3.277(4) | 150 | *x, y, z* |
| | C9-H9…N400 | | 2.52 | 3.460(4) | 169 | *x, ½ -y, ½ +z* |
| | C10-H10…N102 | | 2.61 | 3.555(4) | 171 | *1+x, ½ -y, ½ +z* |
| | C16-H16…N403 | | 2.66 | 3.460(4) | 143 | *x, y, z* |
| | C22-H22…N301 | | 2.53 | 3.407(4) | 153 | *-x, ½ +y, ½ -z* |
| | C26-H26…N204 | | 2.66 | 3.289(4) | 124 | *-x, ½ +y, ½ -z* |
| | C30-H30…N201 | | 2.55 | 3.406(4) | 149 | *-x, 1-y, 1-z* |
| | C32-H32…N203 | | 2.52 | 3.471(4) | 175 | *-x, ½ +y, ½ -z* |
| | C36-H36…N100 | | 2.63 | 3.535(4) | 160 | *-x, ½ +y, ½ -z* |
| | C37-H37…N203 | | 2.68 | 3.409(4) | 134 | *-x, ½ +y, ½ -z* |
| | C45-H45…N200 | | 2.58 | 3.484(4) | 158 | *x, y+1, z* |
| | C50-H50…N400 | | 2.60 | 3.518(4) | 162 | *x, y+1, z* |
| | C59-H59…N401 | | 2.52 | 3.276(4) | 137 | *x, y+1, z* |
| **4** | C2-H2…N105 | 0.95 | 2.52 | 3.208(3) | 129 | *x, y, z* |
| | C6-H6…N101 | 0.95 | 2.62 | 3.347(3) | 134 | *x, y, z* |
| | C11-H11…N203 | 0.95 | 2.68 | 3.505(4) | 145 | *1+x, 1+y, z* |
| | C13-H13…O3B | 0.95 | 2.66 | 3.29(2) | 125 | *x, y, z-1* |
| | C26-H26…N202 | 0.95 | 2.65 | 3.282(4) | 124 | *-x, -y, 1-z* |

| *Compound* | *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* | *Symm. Oper.* |
|---|---|---|---|---|---|---|
| **5** | C201-H201…N24 | 0.95 | 2.65 | 3.587(7) | 171 | *x, 1-y, z-½* |
| | C206-H206…N11 | 0.95 | 2.58 | 3.320(6) | 136 | *x, 1-y, z-½* |
| | C213-H213…N40 | 0.95 | 2.59 | 3.519(7) | 167 | *x, y, z* |
| | C214-H214…N14 | 0.95 | 2.68 | 3.360(7) | 129 | *x, 1-y, z+½* |
| | C215-H215…O34 | 0.95 | 2.66 | 3.330(7) | 128 | *x, y, z* |
| | C218-H218…N61 | 0.95 | 2.67 | 3.595(8) | 166 | *x, y, z* |
| | C219-H219…N31 | 0.95 | 2.68 | 3.256(7) | 119 | *x, y, z* |
| | C220-H220…N64 | 0.95 | 2.59 | 3.327(8) | 135 | *1+x, 1+y, z* |
| | C225-H225…N43 | 0.95 | 2.56 | 3.415(8) | 150 | *x, 1-y, z-½* |
| | C100-H100…N42 | 0.95 | 2.70 | 3.343(7) | 126 | *x, 1+y, z-1* |
| | C106-H106…N63 | 0.95 | 2.67 | 3.519(7) | 150 | *1+x, 1-y, z-½* |
| | C111-H111…N21 | 0.95 | 2.69 | 3.627(9) | 168 | *x, -y, z+½* |
| | C113-H113…N61 | 0.95 | 2.68 | 3.449(8) | 138 | *x, y, z* |
| | C116-H116…N40 | 0.95 | 2.66 | 3.496(8) | 146 | *x, y, z* |
| | C121-H121…N13 | 0.95 | 2.55 | 3.441(8) | 157 | *x, 1-y, z+½* |
| | C123-H123…N52 | 0.95 | 2.66 | 3.573(8) | 163 | *x, 1-y, z-½* |
| | C126-H126…N21 | 0.95 | 2.59 | 3.498(8) | 160 | *x, 1-y, z+½* |
| | C128-H128…N32 | 0.95 | 2.56 | 3.473(7) | 161 | *x, y, z* |
| **6** | C10-H10…N60 | 0.95 | 2.57 | 3.325(6) | 136 | *x, y, z* |
| | C11-H11…N83 | 0.95 | 2.56 | 3.407(6) | 148 | *½+x, ½-y, z-½* |
| | C14-H14…N74 | 0.95 | 2.63 | 3.302(6) | 128 | *1-x, -y, 2-z* |
| | C15-H15…N94 | 0.95 | 2.60 | 3.452(7) | 150 | *1.5-x, y- ½, 1.5-z* |
| | C20-H20…O5 | 0.95 | 2.48 | 3.271(6) | 140 | *x, y, z* |
| | C34-H34…N84 | 0.95 | 2.52 | 3.281(6) | 137 | *x, y, z* |
| | C35-H35…N92 | 0.95 | 2.61 | 3.238(7) | 125 | *x-½, ½-y, ½+z* |
| | C36-H36…N92 | 0.95 | 2.68 | 3.259(7) | 120 | *x-½, ½-y, ½+z* |
| | C39-H39…N82 | 0.95 | 2.69 | 3.422(6) | 134 | *x-½, ½-y, z- ½* |
| | C53-H53…N64 | 0.95 | 2.51 | 3.379(7) | 152 | *x-½, ½-y, ½+z* |

*Table S 3: Experimental details of the data collections*

| Comp. | **1** | **2** | **3** | **4** | **5** | **6** |
|---|---|---|---|---|---|---|
| Empirical formula | $C_{48}$ $H_{44}$ Mg $N_{14}$ $O_6$ | $C_{50}$ $H_{32}$ Ca $N_{16}$ $O_4$ | $C_{58}$ $H_{56}$ $N_{16}$ $O_8$ Sr | $C_{53}$ $H_{44}$ $N_{15}$ $O_4$ Sr | $C_{144}$ $H_{130}$ $Ba_3$ $N_{42}$ $O_{17}$ | $C_{97}$ $H_{74}$ $Ba_2$ $N_{29}$ $O_7$ |
| Formula weight | 937.28 | 960.99 | 1192.80 | 1042.65 | 3132.91 | 2032.53 |
| Temperature | | | 100(2) K | | | |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Triclinic | Monoclinic | Monoclinic |
| Space group | C 2/c | P $2_1$ | P $2_1/c$ | P -1 | P $c$ | P $2_1/n$ |
| $a$ [Å] | 12.9906(6) | 10.1121(3) | 15.0821(6) | 13.7982(6) | 27.3916(10) | 14.6646(6) |
| $b$ | 23.4010(12) | 23.5038(7) | 27.9091(9) | 14.7801(6) | 10.8213(5) | 26.4428(9) |
| $c$ | 16.3198(9) | 1042.02(4) | 28.5444(11) | 16.5180(7) | 24.8908(10) | 24.9814(9) |
| α [°] | 90 | 90 | 90 | 64.558(1) | 90 | 90 |
| ß | 93.304(2) | 101.3760(10) | 96.121(1) | 66.682(1) | 95.662(1) | 91.201(1) |
| γ | 90 | 90 | 90 | 65.115(1) | 90 | 90 |
| Volume [$Å^3$] | 4952.9(4) | 2427.94(14) | 11946.6(8) | 2662.7(2) | 7342.0(5) | 9685.0(6) |
| Z | 4 | 2 | 8 | 2 | 2 | 4 |
| ρ (calc) [g $cm^{-3}$] | 1.257 | 1.315 | 1.326 | 1.300 | 1.417 | 1.394 |
| μ [$mm^{-1}$] | 0.098 | 0.192 | 0.969 | 1.071 | 0.873 | 0.878 |
| Crystal size [$mm^3$] | 0.100 x 0.100 x 0.030 | 0.100 x 0.090 x 0.090 | 0.070 x 0.050 x 0.020 | 0.100 x 0.090 x 0.080 | 0.100 x 0.040 x 0.030 | 0.110 x 0.100 x 0.080 |
| Θ range | 3.004 – 25.053°. | 2.688 – 25.401°. | 2.167 –25.090°. | 2.470 – 25.428°. | 2.927 – 25.090°. | 2.218 – 25.418°. |
| Index ranges | -15≤h≤15, -27≤k≤27, -19≤l≤19 | -12≤h≤12, -28≤k≤28, -12≤l≤12 | -17≤h≤17, -33≤k≤33, -33≤l≤34 | -16≤h≤16, -17≤k≤17, -19≤l≤19 | -32≤h≤32, -12≤k≤12, -28≤l≤29 | -17≤h≤17, -31≤k≤31, -30≤=l≤30 |
| Refl. Coll. | 40090 | 41909 | 136596 | 52710 | 111386 | 158553 |
| Indep. Refl. [$R_{int}$] | 4378 [0.0780] | 8908 [ 0.0417] | 21133 [0.1326] | 9809 [0.0339] | 25549 [0.0429] | 17832 [0.0596] |
| Absorption correction | | | Multi-scan | | | |
| $T_{max}$/ $T_{min}$ | 0.7452/ 0.6575 | 0.7452/ 0.7137 | 0.7452/ 0.6737 | 0.7452/0.7127 | 0.7452 / 0.6848 | 0.7452 / 0.6702 |
| Data / restr. / param. | 4378 / 0 / 327/ | 8908 / 35 / 665 | 21133 / 0 / 1528 | 9809 / 31 / 726 | 25549 / 214 / 1958 | 17832 / 172 / 1288 |
| GOOF on $F^2$ | 1.074 | 1.022 | 0.994 | 1.061 | 1.036 | 1.191 |
| R1/ wR2 [I>2σ(I)] | 0.0535/ 0.1238 | 0.0411/ 0.0930 | 0.0426/ 0.0747 | 0.0377/ 0.0937 | 0.0285/ 0.0596 | 0.0464/ 0.0902 |
| R1/ wR2 (all data) | 0.0905/ 0.1448 | 0.0547/ 0.0998 | 0.0993/ 0.0885 | 0.0471/ 0.0987 | 0.0347/ 0.0612 | 0.0678/ 0.0979 |
| BASF | | 0.45(5) | | | 0.346(8) | |
| Extrema Fourier | 0.706 / -0.387 | 0.649 /* -0.289 | 0.453 /-0.641 | 1.025 /-0.581 | 0.659 / -0.342 | 0.975 / -0.781 |
| CCDC-# | 2213249 | 2213250 | 2213252 | 2213251 | 2213253 | 2213254 |

## 2. FIGURES

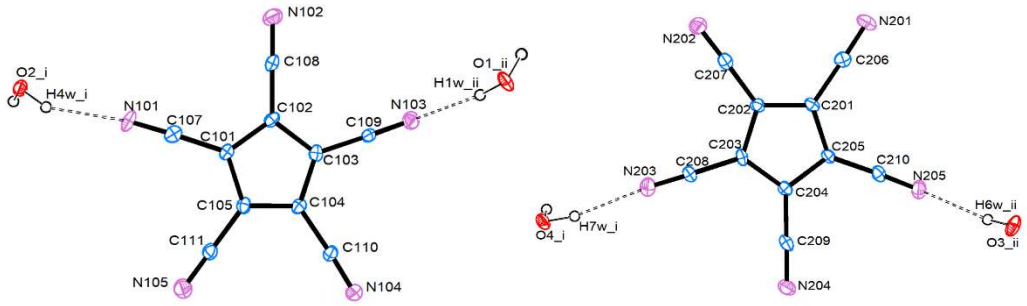


Figure S 1: The pentacyanocyclopentadienides in compound **2** as H-bond acceptors.

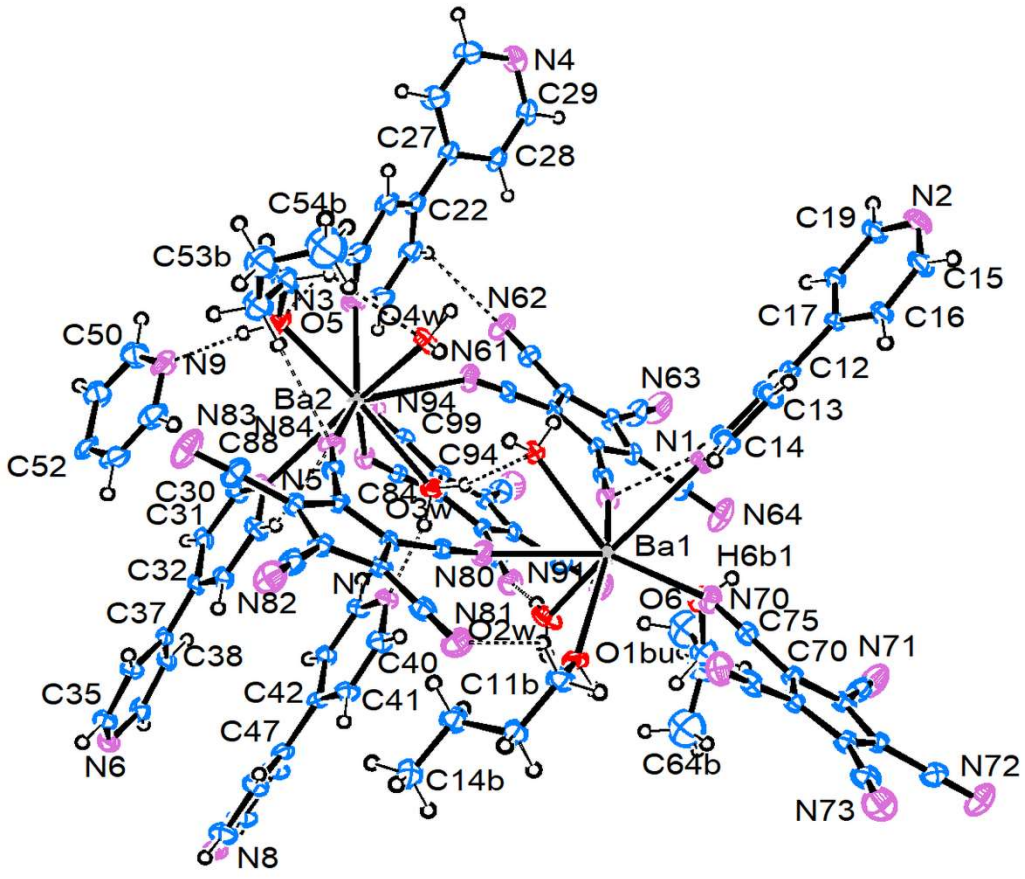


Figure S 2: The asymmetric unit of compound **6**

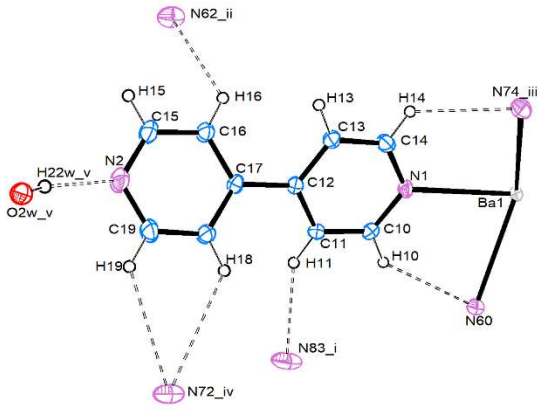


Figure S 3: The hydrogen bonds around bipyridine I (C10-C19, N1/N2)

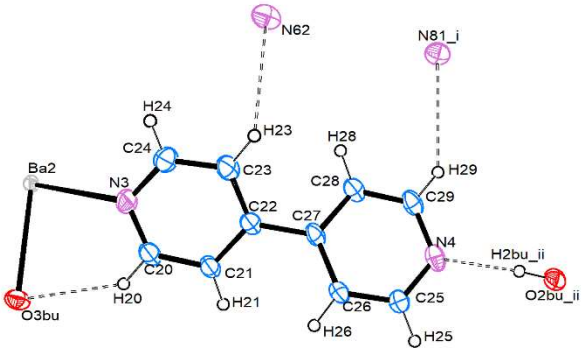


Figure S 4: The hydrogen bonds around bipyridine II (C20-C29, N3/N4

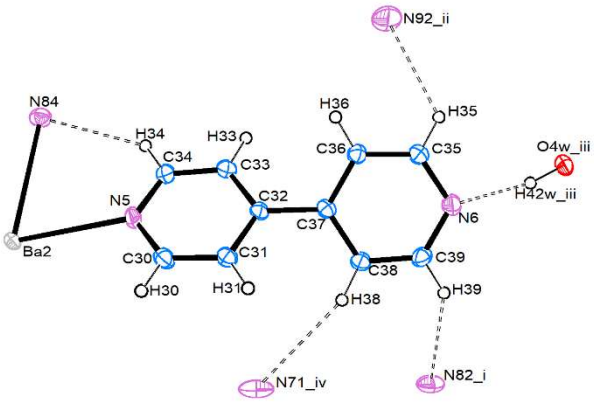


Figure S 5: The hydrogen bonds around bipyridine III (C30-C39, N5/N6

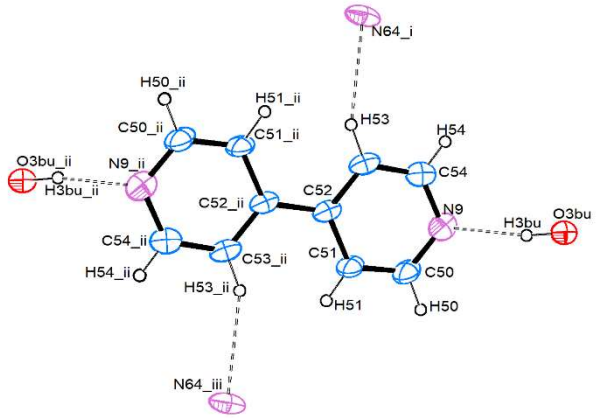


Figure S 6: The hydrogen bonds around bipyridine IV (C50-C54_ii, N9/N9-ii

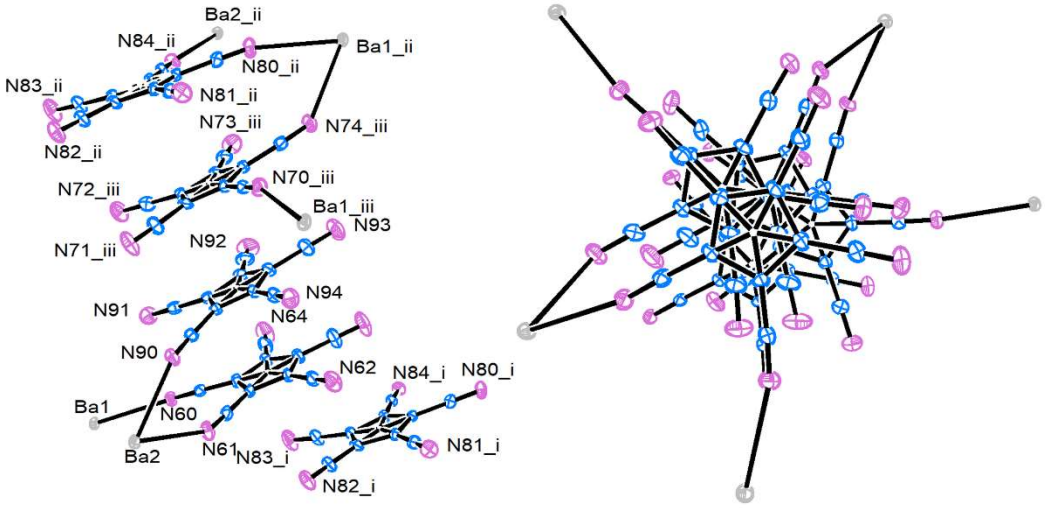


Figure S 7: The π-stacking of pentacyanocyclopentadienides in **6**: side view and top view

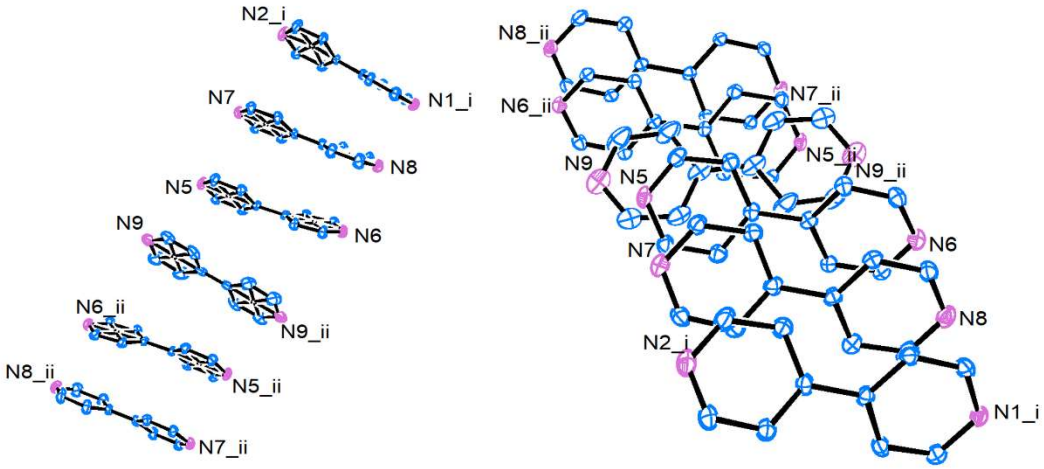


Figure S 8: The π-stacking of bipyridines in **6**: side view and top view.