Electronic Supplementary Material (ESI) for Dalton Transactions
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Supporting Information (SI)

INDUCED CHIRALITY-AT-METAL AND DIASTEREOSELECTIVITY AT Δ/Λ-CONFIGURED DISTORTED SQUARE-PLANAR COPPER COMPLEXES BY ENANTIOPURE SCHIFF BASE LIGANDS: COMBINED CIRCULAR DICHROISM, DFT, AND X-RAY STRUCTURAL STUDIES

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Table S1 Electron impact (EI) and atmospheric pressure chemical ionization (APCI) mass spectral data.

Complex[a]	**Cu-*R*-L1**	**Cu-*S*-L1**	**Cu-*R*-L2**	**Cu-*R*-L3**	**Cu-*S*-L3**	**Cu-*R*-L4**	**Cu-*S*-L4**
Ar	C_6H_5	C_6H_5	*m*-C_6H_4OMe	*p*-C_6H_4OMe	*p*-C_6H_4OMe	*p*-C_6H_4Br	*p*-C_6H_4Br
EI-MS							
$[M]^+$	611	611	671	671	671	769	769
$[M–HL]^+$	336	336	366	366	366	416	416
$[HL]^+$	275	275	305	305	305	353	353
APCI-MS							
$[M_2\text{-}L]^+$	948		1038	1038		1186	
$[M+H]^+$	612		672	672		770	
$[M\text{-}L]^+$	337						
$[HL+H]^+$						354	
$[HL\text{-}H]^+$	274		304	304			

[a] The isotopic distribution patterns for $^{63/65}Cu$ and $^{79/81}Br$ containing ions are visible.

Table S2 Polarimetric data in $CHCl_3$ at 25 ^{0}C.

Entity	**[c]** g/100 mL	$[\alpha]_D$
***R*-HL1**	0.40	–166.7°
***S*-HL1**	0.39	+156.5°
Cu-*R*-L1	0.33	+75.6°
Cu-*S*-L1	0.42	–74.6°
Cu-*R*-L2	0.90	–78.0°

1H-NMR studies of complexes after reaction with KCN

The complexes **Cu-*R*-L1** to **Cu-*R*-L4** react with KCN in dmso-d_6 to give diamagnetic $[Cu(CN)_4]^{3-}$ and deprotonated Schiff base (L^-) species in the reaction mixture, accompanied by a color change from brown to red-orange. Spectra (see next page, Figure S1) show the peaks for the deprotonated Schiff base including a doublet at δ = 1.48-1.50 ppm (J = 6.6 Hz), a quartet at δ = 3.30-3.35 ppm (J = 6.6 Hz) and a singlet at δ = 9.18-9.20 ppm, for CH_3, CH, and CHN, respectively. In addition, a singlet is found at δ = 3.75 ppm for OCH_3 in **Cu-*R*-L3**. In fact, the spectral data correspond well to those found for the free Schiff bases [1] with little changes in chemical shift values.

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1 M. Enamullah, A.K.M. Royhan Uddin, G. Hogarth, C. Janiak, *Inorg. Chim. Acta*, **387**, 173 (2012).

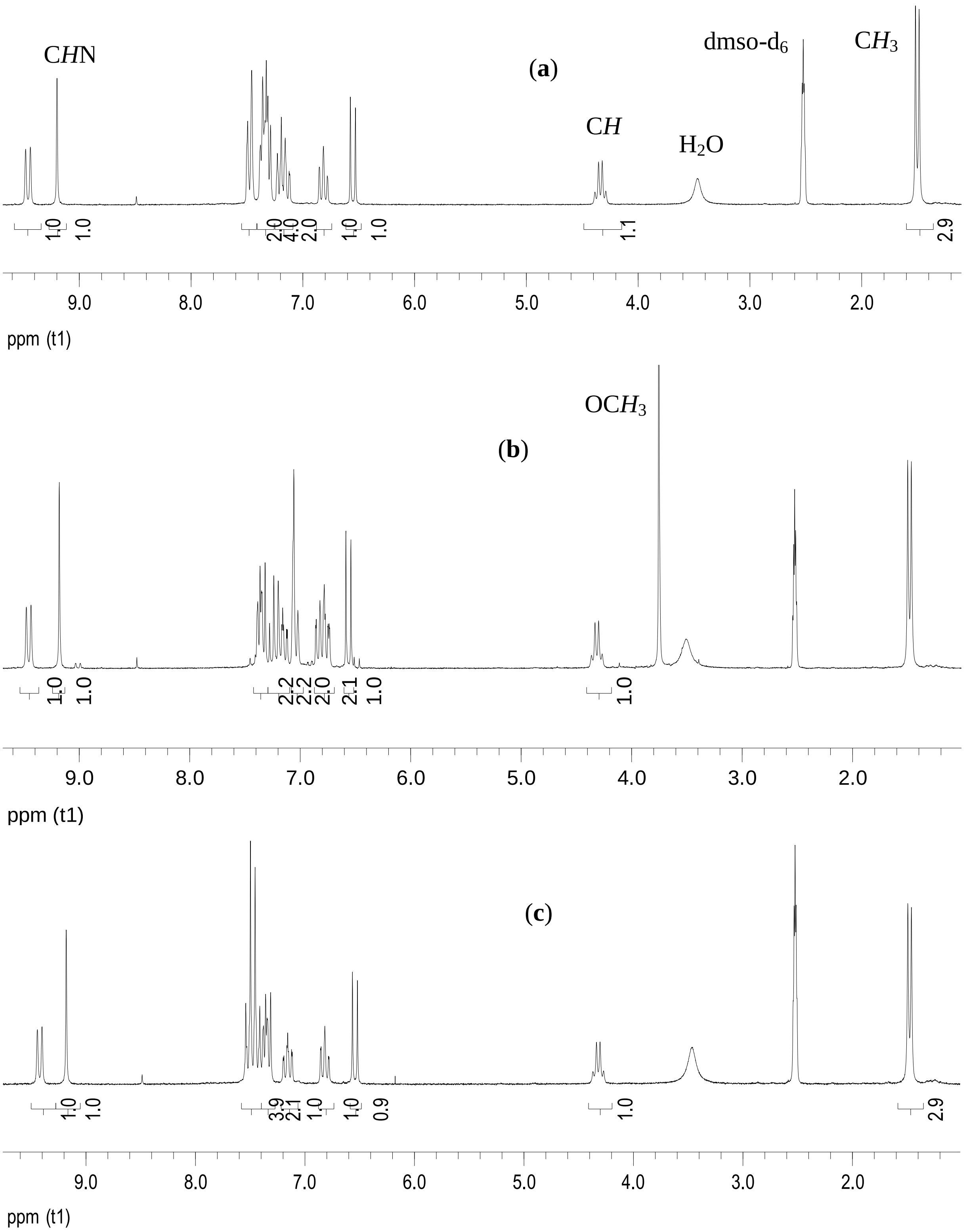
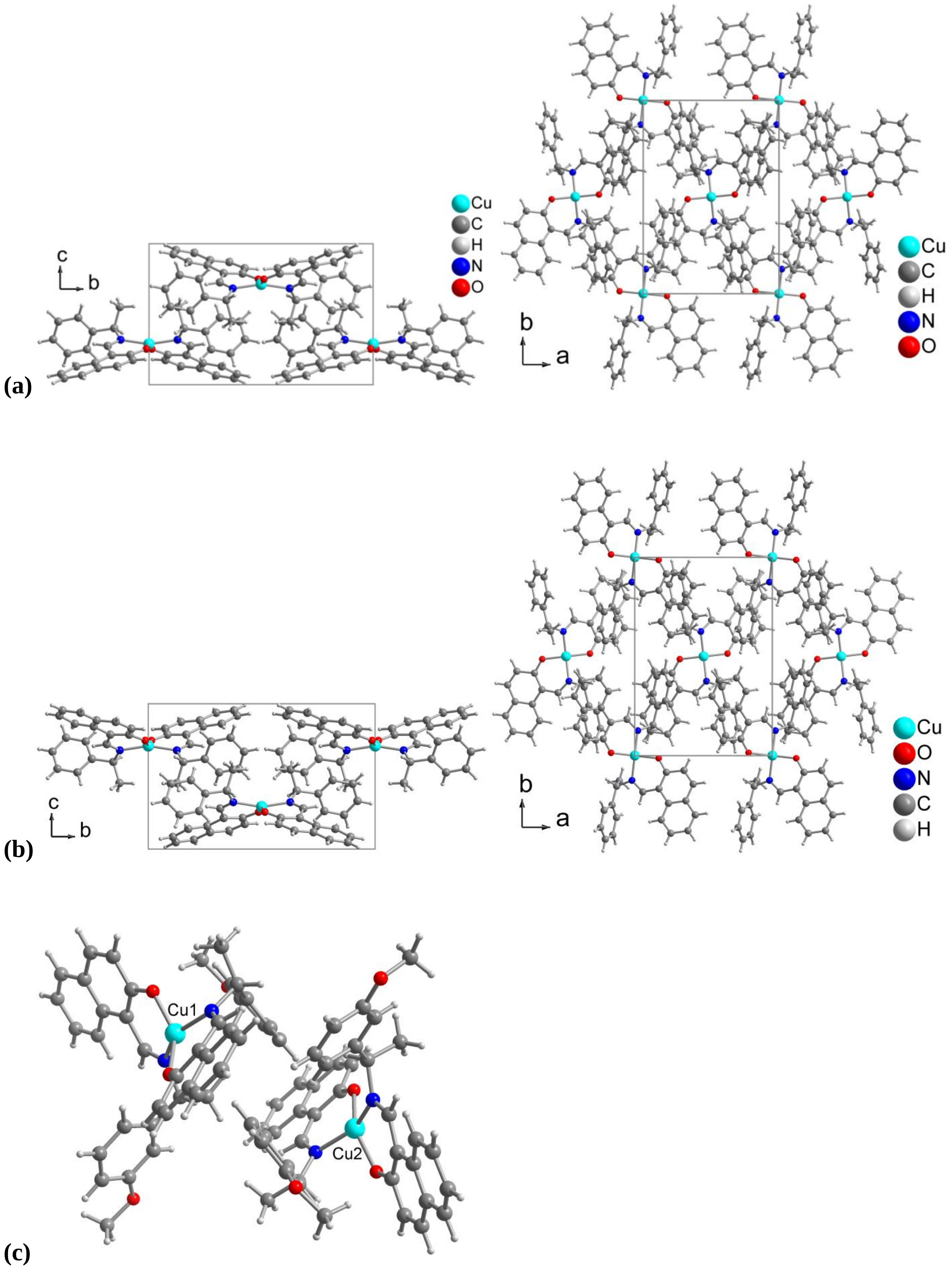


Figure S1. H NMR (200 MHz) spectra from the reaction of Λ/Δ-*bis*[{(*R*)-*N*-(Ar)ethyl-2-oxo-1-naphthaldiminato-κ^2*N*,*O*}]copper(II) complexes: (a) **Cu-*R*-L1** (Ar = C_6H_5), (b) **Cu-*R*-L2** (Ar = *m*-C_6H_4OMe), and (c) **Cu-*R*-L4** (Ar = *p*-C_6H_4Br) with KCN in DMSO-d_6 at 20 ^{o}C.



(a)

(b)

(c)

Figure S2. Sections of the packing diagrams for (a) **Λ-Cu-*R*-L1**, (b) **Δ-Cu-*S*-L1** and (c) **Λ/Δ-Cu-*R*-L2**.

Packing Analyses

Packing Analysis by PLATON ((a) A. Spek, *Acta Crystallographica Section D*, 2009, **65**, 148-155; (b) A. L. Spek *PLATON – A multipurpose crystallographic tool*, Utrecht University: Utrecht, The Netherlands, 2005.)

Despite the presence of ligand π-systems in the **L1** to **L4** ligands and metal complexes thereof, there are no π-π interactions [1] and only few intermolecular C-H···π [2] evident.
The supramolecular packing analyses are tabulated below.

The listed "Analysis of Short Ring-Interactions" for possible π-stacking interactions yielded rather rather long centroid-centroid distances (>4.0 Å) together with non-parallel ring planes (alpha >> 0°) and large slip angles (β, γ > 30°).
In comparison, significant π-stackings show rather short centroid-centroid contacts (<3.8 Å), near parallel ring planes (alpha < 10° to ~0° or even exactly 0° by symmetry), small slip angles (β, γ < 25°) and vertical displacements (slippage < 1.5 Å) which translate into a sizable overlap of the aryl-plane areas.[2,3]

Significant intermolecular C-H···π contacts start around 2.7 Å for the (C-)H···ring centroid distances with H-perp also starting at 2.6-2.7 Å and C-H··Cg > 145°.[2,4,5]
The following Figure shows scatter plots for dependencies of of the C–H…π access angle on the CH/π plane distance.

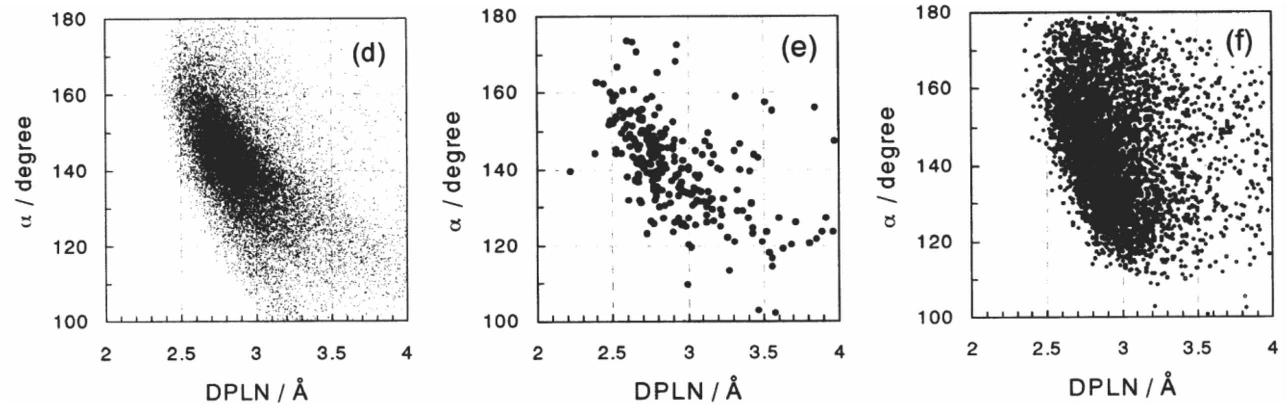
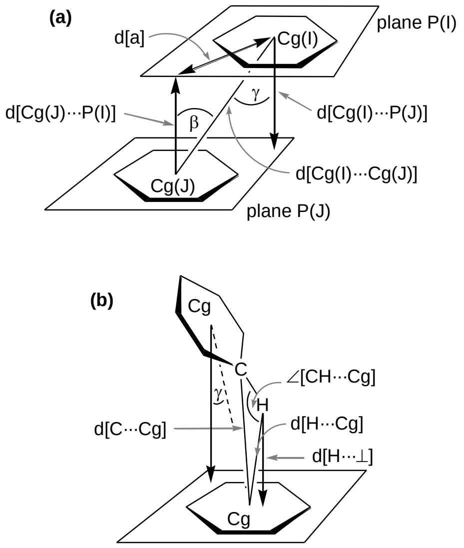


Figure Scatter plots showing dependence of the C–H…π access angle on the CH/π plane distance (copied from ref. 2, copyright Royal Society of Chemistry, 2004) (d) aromatic CH, (e) aromatic CH (neutron data), (f) CCH_3.



Scheme S1 Graphical presentation of the parameters used for the description of (a) π-π stacking and (b) CH-π interactions.

Packing Analysis for **Λ-Cu-*R*-L1** (data set CuR12, 203 K) for possible **π-π interactions:**

```
==================================================================================
Analysis of Short Ring-Interactions with Cg-Cg Distances <   6.0 Angstrom and Beta < 60.0 Deg.
==================================================================================
- Cg(I)    = Plane number I (= ring number in () above)
- Alpha    = Dihedral Angle between Planes I and J (Deg)
- Beta     = Angle Cg(I)-->Cg(J) or Cg(I)-->Me vector and normal to plane I (Deg)
- Gamma    = Angle Cg(I)-->Cg(J) vector and normal to plane J (Deg)
- Cg-Cg    = Distance between ring Centroids (Ang.)
- CgI_Perp = Perpendicular distance of Cg(I) on ring J (Ang.)
- CgJ_Perp = Perpendicular distance of Cg(J) on ring I (Ang.)
- Slippage = Distance between Cg(I) and Perpendicular Projection of Cg(J) on Ring I (Ang).
- P,Q,R,S  = J-Plane Parameters for Carth. Coord. (Xo, Yo, Zo)

Cg(I) Res(I)   Cg(J)  [   ARU(J)]      Cg-Cg      Alpha          Beta     Gamma   CgI_Perp      CgJ_Perp      Slippage

Cg(3)  [ 1] -> Cg(4)  [  3557.01]   5.785(2)    33.39(18)      48.68    81.89     0.8158(16)    3.8196(16)
Cg(3)  [ 1] -> Cg(5)  [  3456.01]   4.649(3)    50.1(2)        19.52    64.15     2.0273(16)    -4.382(2)
Cg(3)  [ 1] -> Cg(5)  [  3457.01]   4.992(3)    50.1(2)        22.29    66.09     -2.0229(16)   4.619(2)
Cg(4)  [ 1] -> Cg(4)  [  3557.01]   5.959(2)    32             51.58    82.43     0.7850(16)    3.7030(16)
Cg(4)  [ 1] -> Cg(5)  [  1455.01]   5.809(3)    83.3(2)        49.06    49.66     3.7600(17)    -3.806(2)
Cg(4)  [ 1] -> Cg(5)  [  3456.01]   5.770(3)    52.5(2)        42.15    65.69     2.3757(17)    -4.278(2)
Cg(4)  [ 1] -> Cg(5)  [  3457.01]   4.902(3)    52.5(2)        18.87    70.03     -1.6745(17)   4.638(2)
Cg(5)  [ 1] -> Cg(4)  [  1555.01]   5.966(3)    83.3(2)        10.03    81.44     -0.888(2)     -5.8750(17)
Cg(5)  [ 1] -> Cg(4)  [  1655.01]   5.809(3)    83.3(2)        49.66    49.06     -3.806(2)     3.7599(17)
                          ----------                 --------------------------------------------
                          Min or Max  4.649        31.71          10.03    82.43     -3.806        -5.875
[  3557] = 1/2+X,1/2-Y,2-Z
[  3456] = -1/2+X,1/2-Y,1-Z
[  3457] = -1/2+X,1/2-Y,2-Z
[  1455] = -1+X,Y,Z
[  1555] = X,Y,Z
[  1655] = 1+X,Y,Z
```

Packing Analysis for **Λ-Cu-*R*-L1** (data set CuR12, 203 K) for possible **CH-π interactions:**

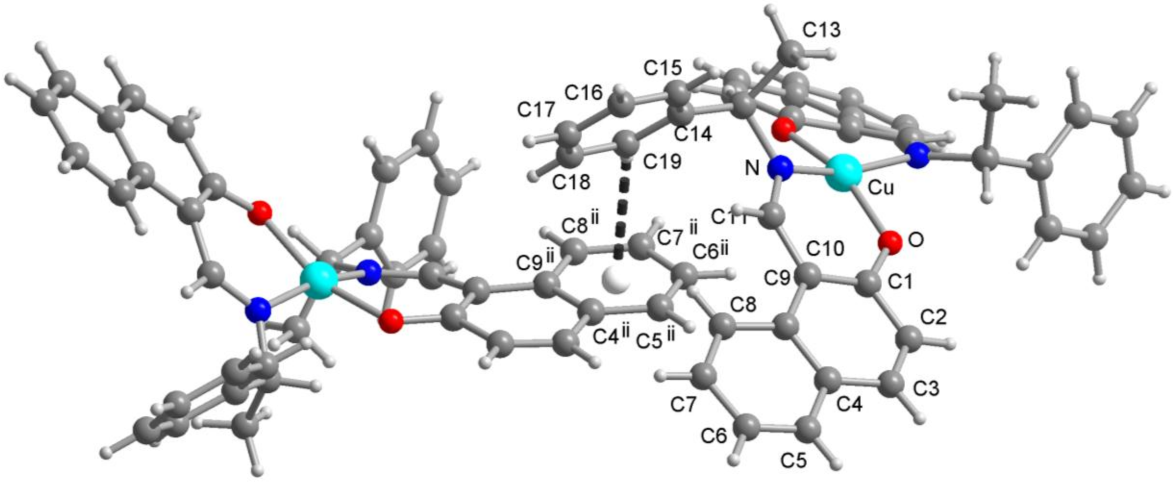
```
==================================================================================
Analysis of X-H...Cg(Pi-Ring) Interactions (H..Cg < 3.0 Ang. - Gamma <  30.0 Deg)
==================================================================================
   X--H(I)    Res(I)   Cg(J)  [    ARU(J)]           H..Cg          H-Perp      Gamma      C-H..Cg     C..Cg

C(13)  -H(13C) [ 1] -> Cg(4)  [  3556.01]       2.99           -2.86        17.00       121           3.595(5)
C(15)  -H(15A) [ 1] -> Cg(3)  [  3556.01]       2.96            -2.95       4.97        124           3.564(5)
C(19)  -H(19A) [ 1] -> Cg(4)  [  3557.01]       2.93           2.92         3.62        138           3.686(5)
                              ----------                --------------------------------------------
                           Min or Max                2.930           -2.946      3.62        138.00        3.564
```

[3556] = 1/2+X,1/2-Y,1-Z
[3557] = 1/2+X,1/2-Y,2-Z

The Cg(I) refer to the Ring Centre-of-Gravity numbers given in
Ring 3: C1-C2-C3-C4-C9-C10
Ring 4: C4-C5-C6-C7-C8-C9
Ring 5: C14-C15-C16-C17-C18-C19

The **CH-π interaction** C(19)-H(19A) [1] -> Cg(4) [3557.01] is illustrated:
(symmetry transformation ii = 1/2+X, 1/2-Y, 2-Z)



Conclusions:
From the key values for significant π-stackings and C-H···π contacts which are given on page S6, neither of the contacts in **Λ-Cu-*R*-L1** (CuR12) can be classified as such.

Packing Analysis for **Λ-Cu-*R*-L1** (data set CuRL1a, 95 K) for possible **π-π interactions:**

```
===========================================================================================
Analysis of Short Ring-Interactions with Cg-Cg Distances <   6.0 Angstrom and Beta < 60.0 Deg.
===========================================================================================
- Cg(I)    = Plane number I (= ring number in () above)
- Alpha    = Dihedral Angle between Planes I and J (Deg)
- Beta     = Angle Cg(I)-->Cg(J) or Cg(I)-->Me vector and normal to plane I (Deg)
- Gamma    = Angle Cg(I)-->Cg(J) vector and normal to plane J (Deg)
- Cg-Cg    = Distance between ring Centroids (Ang.)
- CgI_Perp = Perpendicular distance of Cg(I) on ring J (Ang.)
- CgJ_Perp = Perpendicular distance of Cg(J) on ring I (Ang.)
- Slippage = Distance between Cg(I) and Perpendicular Projection of Cg(J) on Ring I (Ang).
- P,Q,R,S  = J-Plane Parameters for Carth. Coord. (Xo, Yo, Zo)

Cg(I) Res(I)   Cg(J)  [   ARU(J)]      Cg-Cg      Alpha          Beta    Gamma   CgI_Perp      CgJ_Perp  Slippage

Cg(3)  [ 1] -> Cg(4)  [  3557.01]  5.7743(16)   31.23(13)       49.86   80.98     0.9056(12)    3.7228(12)
Cg(3)  [ 1] -> Cg(4)  [  4557.01]  5.9881(15)   27.04(13)       50.69   77.68     1.2780(12)    3.7939(12)
Cg(3)  [ 1] -> Cg(5)  [  3456.01]  4.6475(17)   52.01(15)       18.83   65.26     1.9448(11)   -4.3987(13)
Cg(3)  [ 1] -> Cg(5)  [  3457.01]  4.9334(17)   52.01(15)       21.35   67.05    -1.9236(11)   4.5948(13)
Cg(4)  [ 1] -> Cg(4)  [  3557.01]  5.9646(17)   29              53.08   81.51     0.8804(12)    3.5827(12)
Cg(4)  [ 1] -> Cg(5)  [  1455.01]  5.7920(19)   83.14(15)       50.52   48.39     3.8466(12)   -3.6830(13)
Cg(4)  [ 1] -> Cg(5)  [  3456.01]  5.7775(17)   54.68(15)       42.10   66.87     2.2700(12)   -4.2867(13)
Cg(4)  [ 1] -> Cg(5)  [  3457.01]  4.8528(17)   54.68(15)       17.88   70.77    -1.5985(12)   4.6183(13)
Cg(5)  [ 1] -> Cg(4)  [  1555.01]  5.9902(19)   83.14(15)       10.05   80.58    -0.9806(13)   -5.8983(12)
Cg(5)  [ 1] -> Cg(4)  [  1655.01]  5.7920(19)   83.14(15)       48.39   50.52    -3.6830(13)   3.8466(12)
                           ----------                 -------------------------------------------
                          Min or Max  4.648      27.04           10.05   81.51    -3.683        -5.898

[  3557] = 1/2+X,1/2-Y,2-Z
[  4557] = 1/2-X,1/2+Y,2-Z
[  3456] = -1/2+X,1/2-Y,1-Z
[  3457] = -1/2+X,1/2-Y,2-Z
[  1455] = -1+X,Y,Z
```

```
[  1555] = X,Y,Z
[  1655] = 1+X,Y,Z
```

Packing Analysis for **Λ-Cu-*R*-L1** (data set CuRL1a, 95 K) for possible **CH-π interactions:**

```
=============================================================================================
Analysis of X-H...Cg(Pi-Ring) Interactions (H..Cg < 3.0 Ang. - Gamma <  30.0 Deg)
=============================================================================================

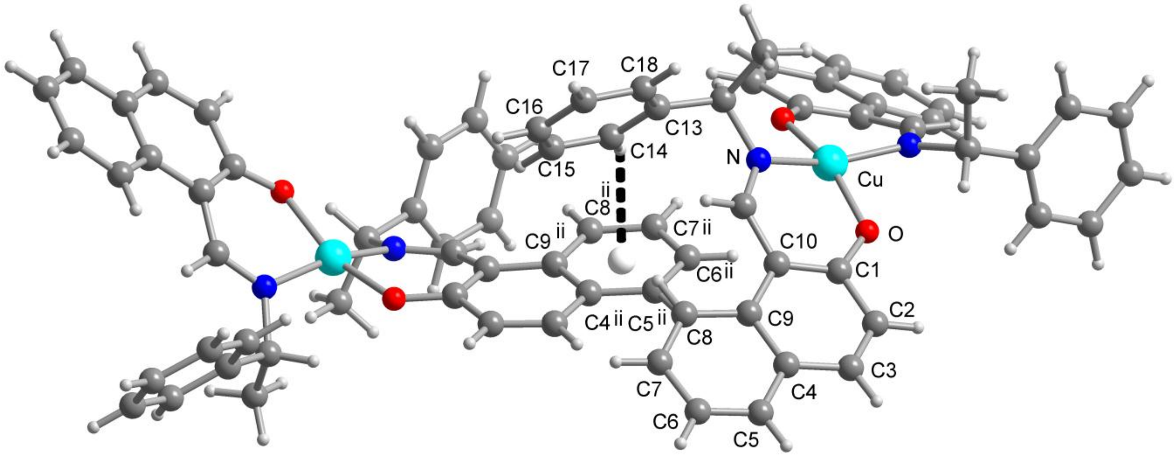
   X--H(I)    Res(I)   Cg(J)  [    ARU(J)]          H..Cg        H-Perp     Gamma     X-H..Cg    X..Cg

C(14)  -H(14)  [ 1] -> Cg(4)  [  3557.01]          2.83         2.83       2.92      140        3.613(3)
C(18)  -H(18)  [ 1] -> Cg(3)  [  3556.01]          2.89         -2.88      5.55      125        3.526(3)
C(19)  -H(19A) [ 1] -> Cg(4)  [  3556.01]          2.94         -2.84      15.36     123        3.574(4)
                                ----------                 ---------------------------------------------
                          Min or Max               2.830        -2.881     2.92      140.00     3.526

[  3557] = 1/2+X,1/2-Y,2-Z
[  3556] = 1/2+X,1/2-Y,1-Z
```

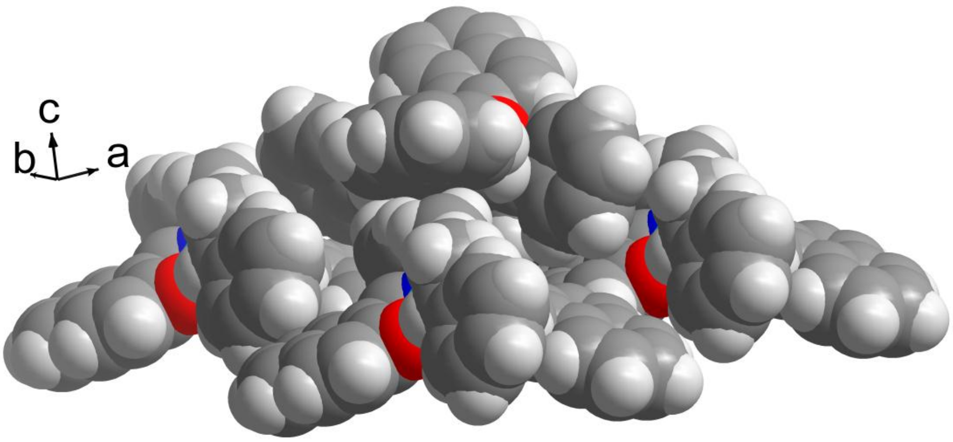
The Cg(I) refer to the Ring Centre-of-Gravity numbers given in
Ring 3: C1-C2-C3-C4-C9-C10
Ring 4: C4-C5-C6-C7-C8-C9
Ring 5: C13-C14-C15-C16-C17-C18

The **CH-π interaction** C(14)-H(14) [1] -> Cg(4) [3557.01] is illustrated:
(symmetry transformation ii = 1/2+X, 1/2-Y, 2-Z)



Conclusions for **Λ-Cu-*R*-L1:**
From the key values for significant π-stackings and C-H···π contacts which are given on page S6, neither of the contacts in **Λ-Cu-*R*-L1** (data set CuRL1a, 95 K) can be classified as such. Noteworthy, these supramolecular interactions do not change much from the 203 K to the 95 K data set.

In the absence of significant π-stackings and C-H···π contacts the packing interactions may be reasoned as a van-der-Waals packing of the molecules as shown for **Λ-Cu-*R*-L1** (data set CuRL1a):



Such as van-der-Waals packing does not allow to understand if a diastereomeric mixture would not also be possible.

Packing Analysis for **Λ/Δ-Cu-*R*-L2** (data set CuR14a, 203 K) for possible **π-π interactions:**

```
==========================================================================================
Analysis of Short Ring-Interactions with Cg-Cg Distances <   6.0 Angstrom and Beta < 60.0 Deg.
==========================================================================================
- Cg(I)    = Plane number I (= ring number in () above)
- Alpha    = Dihedral Angle between Planes I and J (Deg)
- Beta     = Angle Cg(I)-->Cg(J) or Cg(I)-->Me vector and normal to plane I (Deg)
- Gamma    = Angle Cg(I)-->Cg(J) vector and normal to plane J (Deg)
- Cg-Cg    = Distance between ring Centroids (Ang.)
- CgI_Perp = Perpendicular distance of Cg(I) on ring J (Ang.)
- CgJ_Perp = Perpendicular distance of Cg(J) on ring I (Ang.)
- Slippage = Distance between Cg(I) and Perpendicular Projection of Cg(J) on Ring I (Ang).
- P,Q,R,S  = J-Plane Parameters for Carth. Coord. (Xo, Yo, Zo)

Cg(I) Res(I)   Cg(J)  [   ARU(J)]      Cg-Cg      Alpha          Beta     Gamma   CgI_Perp      CgJ_Perp      Slippage

Cg(3)  [ 1] -> Cg(14) [  1545.02]    4.768(2)     6.90(16)       41.86    48.64      3.1507(13)    -3.5509(15)
Cg(3)  [ 1] -> Cg(15) [  1555.02]    4.986(2)    75.16(17)       17.88    80.68      0.8071(14)    4.7448(15)
Cg(4)  [ 1] -> Cg(8)  [  1554.01]    5.153(2)    51.13(17)       57.89    37.04      4.1133(15)    2.7396(14)
Cg(4)  [ 1] -> Cg(12) [  1545.02]  4.5980(18)    44.63(13)       58.89    14.27      4.4561(14)    -2.3754(11)
Cg(4)  [ 1] -> Cg(18) [  1555.02]    5.646(2)    40.92(16)       46.54    80.29      0.9519(14)    3.8834(14)
Cg(5)  [ 1] -> Cg(6)  [  1555.01]    5.765(2)    37.58(17)       52.78    54.31      3.3635(15)    3.4875(13)
Cg(5)  [ 1] -> Cg(15) [  1655.02]    4.412(2)    5.51(18)        35.11    40.50      3.3553(16)    -3.6098(16)
Cg(6)  [ 1] -> Cg(5)  [  1555.01]    5.765(2)    37.58(17)       54.31    52.78      3.4876(13)    3.3634(15)
Cg(6)  [ 1] -> Cg(8)  [  1655.01]    5.245(2)    82.85(17)       30.39    52.76      -3.1743(13)   4.5246(15)
Cg(6)  [ 1] -> Cg(13) [  1545.02]    5.669(2)    63.62(17)       21.18    84.80      0.5138(13)    -5.2860(17)
Cg(6)  [ 1] -> Cg(14) [  1545.02]    5.906(2)    62.14(16)       31.73    83.64      0.6546(13)    -5.0233(15)
Cg(6)  [ 1] -> Cg(17) [  1646.02]    5.442(2)    21.95(16)       54.18    32.26      4.6019(13)    -3.1845(14)
Cg(7)  [ 1] -> Cg(8)  [  1655.01]    4.907(2)    81.74(17)       20.89    70.17      -1.6645(14)   4.5841(15)
Cg(7)  [ 1] -> Cg(16) [  1646.02]  4.8759(19)    21.57(15)       59.82    39.22      3.7773(14)    -2.4514(12)
Cg(7)  [ 1] -> Cg(17) [  1646.02]    4.117(2)    22.24(16)       40.36    22.50      3.8033(14)    -3.1367(14)
Cg(8)  [ 1] -> Cg(4)  [  1556.01]    5.153(2)    51.13(17)       37.04    57.89      2.7395(14)    4.1133(15)
Cg(8)  [ 1] -> Cg(6)  [  1455.01]    5.245(2)    82.85(17)       52.76    30.39      4.5246(15)    -3.1743(13)
Cg(8)  [ 1] -> Cg(18) [  1556.02]    5.715(2)    12.30(18)       50.43    61.06      -2.7657(15)   3.6405(14)
Cg(12) [ 2] -> Cg(3)  [  1565.01]  4.8540(18)    4 44.74(13)     31.08    61.00      -2.3530(11)   4.1572(13)
Cg(12) [ 2] -> Cg(4)  [  1565.01]  4.5980(18)    44.63(13)       14.27    58.89      -2.3754(11)   4.4561(14)
Cg(12) [ 2] -> Cg(15) [  1555.02]  4.0254(19)    37.74(15)       12.53    34.73      -3.3081(11)   -3.9295(15)
Cg(13) [ 2] -> Cg(8)  [  1565.01]    5.034(2)    53.05(19)       12.17    63.68      2.2316(18)    4.9205(14)
Cg(14) [ 2] -> Cg(3)  [  1565.01]    4.768(2)    6.90(16)        48.64    41.86      -3.5509(15)   3.1506(13)
Cg(14) [ 2] -> Cg(5)  [  1555.01]    4.993(2)    82.88(18)       17.89    87.40      -0.2263(17)   -4.7510(15)
Cg(14) [ 2] -> Cg(8)  [  1565.01]    5.750(2)    53.88(18)       30.82    82.69      0.7315(16)    4.9384(14)
Cg(15) [ 2] -> Cg(5)  [  1455.01]    4.413(2)    5.51(18)        40.50    35.11      -3.6098(16)   3.3554(16)
Cg(15) [ 2] -> Cg(12) [  1555.02]  4.0254(19)    37.74(15)       34.73    12.53      -3.9295(15)   -3.3081(11)
Cg(15) [ 2] -> Cg(16) [  1555.02]  5.0833(19)    32.73(16)       52.65    39.12      -3.9440(15)   -3.0839(12)
Cg(15) [ 2] -> Cg(18) [  1555.02]    5.254(2)    85.47(18)       26.30    82.17      -0.7162(16)   -4.7101(14)
Cg(16) [ 2] -> Cg(4)  [  1565.01]    5.666(2)    47.48(15)       37.24    79.16      -1.0658(12)   4.5112(14)
Cg(16) [ 2] -> Cg(7)  [  1464.01]  4.8759(19)    21.57(15)       39.22    59.82      -2.4513(12)   3.7773(14)
```

```
Cg(16) [ 2] -> Cg(15) [  1555.02]  5.0833(19)  32.73(16)    39.12   52.65     -3.0839(12)  -3.9440(15)
Cg(17) [ 2] -> Cg(6)  [  1464.01]   5.442(2)   21.95(16)    32.26   54.18     -3.1846(14)  4.6020(13)
Cg(17) [ 2] -> Cg(7)  [  1464.01]   4.117(2)   22.24(16)    22.50   40.36     -3.1367(14)  3.8033(14)
Cg(18) [ 2] -> Cg(5)  [  1555.01]   5.983(2)   89.68(18)    39.18   74.18     -1.6314(14)  4.6384(16)
Cg(18) [ 2] -> Cg(12) [  1555.02]  4.8034(18)  74.39(14)    59.18   70.35     -1.6156(14)  -2.4609(11)
Cg(18) [ 2] -> Cg(17) [  1555.02]   5.942(2)   75.38(17)    15.09   80.98     -0.9315(14)  -5.7374(14)
                          ----------               ----------------------------------------------
                   Min or Max       4.025      5.51         12.17   87.40     -3.944        -5.737

[  1545] = X,-1+Y,Z
[  1555] = X,Y,Z
[  1554] = X,Y,-1+Z
[  1555] = X,Y,Z
[  1655] = 1+X,Y,Z
[  1655] = 1+X,Y,Z
[  1646] = 1+X,-1+Y,1+Z
[  1556] = X,Y,1+Z
[  1455] = -1+X,Y,Z
[  1556] = X,Y,1+Z
[  1565] = X,1+Y,Z
[  1464] = -1+X,1+Y,-1+Z
```

Packing Analysis for **Λ/Δ-Cu-*R*-L2** (data set CuR14a, 203 K) for possible **CH-π interactions:**

```
=====================================================================================
Analysis of X-H...Cg(Pi-Ring) Interactions (H..Cg < 3.0 Ang. - Gamma <  30.0 Deg)
=====================================================================================

  X--H(I)    Res(I)   Cg(J)  [   ARU(J)]           H..Cg          H-Perp      Gamma      X-H..Cg      X..Cg

C(5)   -H(5A)  [ 1] -> Cg(12) [  1545.02]        2.90           2.83        13.38       123          3.509(4)
C(20)  -H(20A) [ 1] -> Cg(8)  [  1655.01]        2.90           -2.90       4.14        146          3.751(5)
C(33)  -H(33A) [ 1] -> Cg(5)  [  1555.01]        2.86           2.58        25.42       167          3.808(4)
C(60)  -H(60B) [ 2] -> Cg(16) [  1555.02]        2.75           -2.69       12.01       164          3.691(4)
                                ----------                 ---------------------------------------------
                         Min or Max              2.750          -2.897      4.14        167.00       3.509

[  1545] = X,-1+Y,Z
[  1655] = 1+X,Y,Z
[  1555] = X,Y,Z
[  1555] = X,Y,Z

The Cg(I) refer to the Ring Centre-of-Gravity numbers given in
Ring 5: C14-C15-C16-C17-C18-C19
Ring 15: C54-C55-C56-C57-C58-C59
Ring 16: C61-C62-C63-C68-C69-C70
```

Conclusions for **Λ/Δ-Cu-*R*-L2:**

One symmetrically unique near parallel π-π ring arrangement can be seen with an interplanar angle of 5.5° (highlighted in yellow). Yet, the centroid-centroid distance is rather long (>4.0 Å) together with large slip angles (β, γ > 30°) so that there is no effective π-overlap.

Two C-H···π contacts (highlighted in yellow) approach the criteria for significant intermolecular C-H···π contacts which start around 2.7 Å for the (C-)H···ring centroid distances with H-perp also starting at 2.6-2.7 Å and C-H··Cg > 145°.[2,4,5]

Packing Analysis for **Λ-Cu-*R*-L4** (data set CuRL4) for possible **π-π interactions:**

```
======================================================================================
Analysis of Short Ring-Interactions with Cg-Cg Distances <   6.0 Angstrom and Beta < 60.0Deg.
======================================================================================
- Cg(I)    = Plane number I (= ring number in () above)
- Alpha    = Dihedral Angle between Planes I and J (Deg)
- Beta     = Angle Cg(I)-->Cg(J) or Cg(I)-->Me vector and normal to plane I (Deg)
- Gamma    = Angle Cg(I)-->Cg(J) vector and normal to plane J (Deg)
- Cg-Cg    = Distance between ring Centroids (Ang.)
- CgI_Perp = Perpendicular distance of Cg(I) on ring J (Ang.)
- CgJ_Perp = Perpendicular distance of Cg(J) on ring I (Ang.)
```

```
- Slippage = Distance between Cg(I) and Perpendicular Projection of Cg(J) on Ring I (Ang).
- P,Q,R,S  = J-Plane Parameters for Carth. Coord. (Xo, Yo, Zo)

Cg(I) Res(I)   Cg(J)  [   ARU(J)]      Cg-Cg      Alpha         Beta    Gamma  CgI_Perp      CgJ_Perp      Slippage

Cg(3)  [ 1] -> Cg(3)  [  1545.01]  5.603(10)   0             57.44   57.44    -3.015(6)     3.015(6)      4.722
Cg(3)  [ 1] -> Cg(3)  [  1565.01]  5.602(10)   0             57.44   57.44    3.015(6)      -3.015(6)     4.721
Cg(3)  [ 1] -> Cg(3)  [  2746.01]   4.890(9)   65            5.31    67.73    1.853(6)      4.869(6)
Cg(3)  [ 1] -> Cg(8)  [  1545.01]   4.585(9)   62.4(7)       55.80   8.64     4.532(6)      -2.577(6)
Cg(3)  [ 1] -> Cg(8)  [  1555.01]  5.749(10)   62.4(7)       13.44   72.03    1.774(6)      -5.592(6)
Cg(4)  [ 1] -> Cg(4)  [  1545.01]  5.602(10)   0             58.11   58.11    2.960(6)      -2.959(6)     4.757
Cg(4)  [ 1] -> Cg(4)  [  1565.01]  5.602(10)   0             58.11   58.11    -2.959(6)     2.960(6)      4.757
Cg(4)  [ 1] -> Cg(4)  [  2757.01]   5.488(9)   64            22.55   67.40    2.110(6)      5.069(6)
Cg(4)  [ 1] -> Cg(6)  [  1565.01]  5.656(10)   3.3(7)        57.81   60.93    -2.748(6)     3.014(6)
Cg(4)  [ 1] -> Cg(6)  [  2757.01]   4.523(9)   61.7(7)       3.39    60.73    2.212(6)      4.515(6)
Cg(4)  [ 1] -> Cg(7)  [  1545.01]   5.755(9)   1.5(7)        59.55   60.83    2.806(6)      -2.916(6)
Cg(5)  [ 1] -> Cg(7)  [  1545.01]   5.128(9)   84.4(7)       3.60    81.43    -0.763(7)     -5.118(6)
Cg(5)  [ 1] -> Cg(8)  [  2646.01]   5.934(9)   53.1(7)       53.66   74.85    -1.552(7)     -3.516(6)
Cg(6)  [ 1] -> Cg(4)  [  2757.01]   5.076(9)   61.7(7)       10.45   72.15    1.555(6)      4.992(6)
Cg(6)  [ 1] -> Cg(6)  [  2757.01]   5.199(9)   59            28.88   70.06    1.773(6)      4.553(6)
Cg(7)  [ 1] -> Cg(3)  [  1565.01]   5.346(9)   64.5(7)       34.56   67.88    -2.012(6)     4.403(6)
Cg(7)  [ 1] -> Cg(5)  [  1555.01]  5.703(10)   84.4(7)       49.29   62.47    -2.635(6)     -3.720(7)
Cg(7)  [ 1] -> Cg(7)  [  1545.01]  5.602(10)   0             58.15   58.15    2.957(6)      -2.956(6)     4.759
Cg(7)  [ 1] -> Cg(7)  [  1565.01]  5.602(10)   0             58.15   58.15    -2.956(6)     2.956(6)      4.759
Cg(7)  [ 1] -> Cg(8)  [  1545.01]  5.775(10)   3.8(7)        58.31   61.81    2.727(6)      -3.033(6)
Cg(7)  [ 1] -> Cg(8)  [  2646.01]   4.890(9)   61.4(7)       19.58   64.54    -2.102(6)     -4.606(6)
Cg(8)  [ 1] -> Cg(3)  [  1565.01]   4.584(9)   62.4(7)       8.64    55.80    -2.576(6)     4.532(6)
Cg(8)  [ 1] -> Cg(7)  [  2646.01]   5.283(9)   61.4(7)       23.05   71.79    -1.651(6)     -4.861(6)
Cg(8)  [ 1] -> Cg(8)  [  2646.01]   4.618(9)   59            10.50   67.30    -1.783(6)     -4.541(6)
                          ----------               --------------------------------------------
                    Min or Max   4.523      0.00          3.39    81.43    -3.015        -5.592

[  1545] = X,-1+Y,Z
[  1565] = X,1+Y,Z
[  2746] = 2-X,-1/2+Y,1-Z
[  1555] = X,Y,Z
[  2757] = 2-X,1/2+Y,2-Z
[  2646] = 1-X,-1/2+Y,1-Z
```

Packing Analysis for **Λ-Cu-*R*-L4** (data set CuRL4) for possible **CH-π interactions:**

```
=========================================================================================
Analysis of X-H...Cg(Pi-Ring) Interactions (H..Cg < 3.0 Ang. - Gamma <  30.0 Deg)
=========================================================================================
- Cg(J)   = Center of gravity of ring J (Plane number above)
- H-Perp  = Perpendicular distance of H to ring plane J
- Gamma   = Angle between Cg-H vector and ring J normal
- X-H..Cg = X-H-Cg angle (degrees)
- X..Cg   = Distance of X to Cg (Angstrom)
- X-H, Pi = Angle of the X-H bond with the Pi-plane (i.e.' Perpendicular = 90 degrees, Parallel = 0 degrees)

   X--H(I)    Res(I)   Cg(J)  [   ARU(J)]        H..Cg          H-Perp      Gamma      X-H..Cg    X..Cg

C(16)  -H(6)   [ 1] -> Cg(6)  [  1565.01]        2.76           -2.62       18.68      169        3.730(17)
C(19)  -H(13)  [ 1] -> Cg(4)  [  2747.01]        2.82           2.55        25.54      122        3.423(16)
C(32)  -H(18)  [ 1] -> Cg(8)  [  2656.01]        2.64           -2.58       11.95      138        3.402(16)
                             ----------                 ---------------------------------------------
                        Min or Max               2.640          -2.617      11.95      169.00     3.402

[  1565] = X,1+Y,Z
[  2747] = 2-X,-1/2+Y,2-Z
[  2656] = 1-X,1/2+Y,1-Z
```

Conclusions for **Λ-Cu-*R*-L4:**

There are parallel (by symmetry) or near parallel π-π ring arrangements with an interplanar angle of 0° or <5° (highlighted in yellow). Yet, this parallel arrangement coincides with long centroid-centroid distances (>5.6 Å) together with large slip angles (β, γ > 57°) so that there is no effective

π-overlap. For the exactly parallel aryl rings (by symmetry) this can also be seen from the slippage of 4.76 Å which corresponds to the horizontal displacement of the centroids (cf. Scheme S1).
Two C-H···π contacts (highlighted in yellow) approach the criteria for significant intermolecular C-H···π contacts which start around 2.7 Å for the (C-)H···ring centroid distances with H-perp also starting at 2.6-2.7 Å and C-H··Cg > 145°.[2,4,5]

Packing coefficient[6] (or packing index)

The packing coefficients for the majority of crystals are between 0.65-0.77 as for the close-packing of spheres and ellipsoids.[6]
The analysis of molecular packing carried out by Kitaigorodskii and others suggested the conclusion that "the mutual arrangement of the molecules in a crystal is always such that the "projections" of one molecule fit into the "hollows" of adjacent molecules. ... The statement that the real structure is one of the most closely packed of all conceivable patterns seems realistic enough".[6]
From an analysis of possible arrays of molecules without symmetry elements, the closest packing can be achieved in the following space groups: $P1$, $P2_1$, $P2_1/c$, Pca, Pna, $P2_12_12_1$.[6]
Here all compounds (**Λ-** or **Δ)-Cu-(*R*** or ***S*)-L$_i$** (i = 1-4) in principle have a two-fold symmetry. Such molecules can be packed with maximum density in groups $C2/c$, $P2_12_12$ and $Pbcn$.
Compounds **Λ-Cu-*R*-L1** and **Δ-Cu-*S*-L1** crystallize in space group $P2_12_12$ (Table 5), compound **Λ/Δ-Cu-*R*-L2** in $P1$ and **Λ-Cu-*R*-L4** in $P2_1$ (Table 6). However, crystallographically the two-fold molecular symmetry is retained in the solid state only in **Λ-Cu-*R*-L1** and **Δ-Cu-*S*-L1** where the Cu atom sits on a special position with the 2_1 axis passing through the molecule. In **Λ/Δ-Cu-*R*-L2** and in **Λ-Cu-*R*-L4** the unsymmetric orientation of the $–C_6H_4OMe$ and $–C_6H_4Br$ groups, respectively, in the solid-state does not coincide with two-fold crystal symmetry.
The packing index can be calculated with the "calc void" command using PLATON[7] and is given in the following Table.

Table S3 Packing coefficients.

Compound	Temperature /K	Space group	Packing coefficient[a]	Total pot. solv void /Å^3	Total pot. solv void /%
Λ-Cu-*R*-L1					
data set CuR12	203(2)	$P2_12_12$	0.63	61.7	3.9
CuRL1a	95(2)	$P2_12_12$	0.64	32.0	2.1
Δ-Cu-*S*-L1					
data set CuSL1-II	296(2)	$P2_12_12$	0.62	90.2	5.6
CuSL1-III	296(2)	$P2_12_12$	0.62	87.7	5.5
Λ/Δ-Cu-*R*-L2					
data set CuR14a	203(2)	$P1$	0.665	none	none
CuRL2-LT	100(2)	$P1$	0.68	none	none
Λ-Cu-*R*-L4	150(2)	$P2_1$	0.69	none	none

[a] Calculated as packing index with PLATON[7] using the "calc void" command.

Noteworthy, the packing coefficient of **Λ-Cu-*R*-L1** and **Δ-Cu-*S*-L1** is smaller than 0.65 and there is surplus "empty space" on the order of 2.1-5.6% (depending on temperature).
This can be reasoned twofold

(i) In order to achieve a closer packing, the molecule would have to give up its two-fold molecular symmetry. This is the case in the structures of **Λ/Δ-Cu-*R*-L2** and in **Λ-Cu-*R*-L4** where packing coefficients of 0.66-0.69 were attained.
(ii) In the data set of CuRL1a we could refine the largest residual Q1 peak to an oxygen atom (of a presumed crystal water molecule) with an occupation factor of 0.13 per formula unit. A water molecule of crystallization might have been almost fully lost upon crystal drying. The presence of absence of small amounts of crystal water can have little structural effects (see H. H. Monfared, A.-C. Chamayou, S. Khajeh and C. Janiak, *CrystEngComm*, 2010, **12**, 3526-3530.).
A hydrogen-bonded H_2O molecule requires about 40 Å^3. For the data set of CuRL1a a freshly prepared crystal was used. In the CuR12 data set and in the room temperature data sets of Cu-*S*-L1 no significant residual electron was found in the voids.

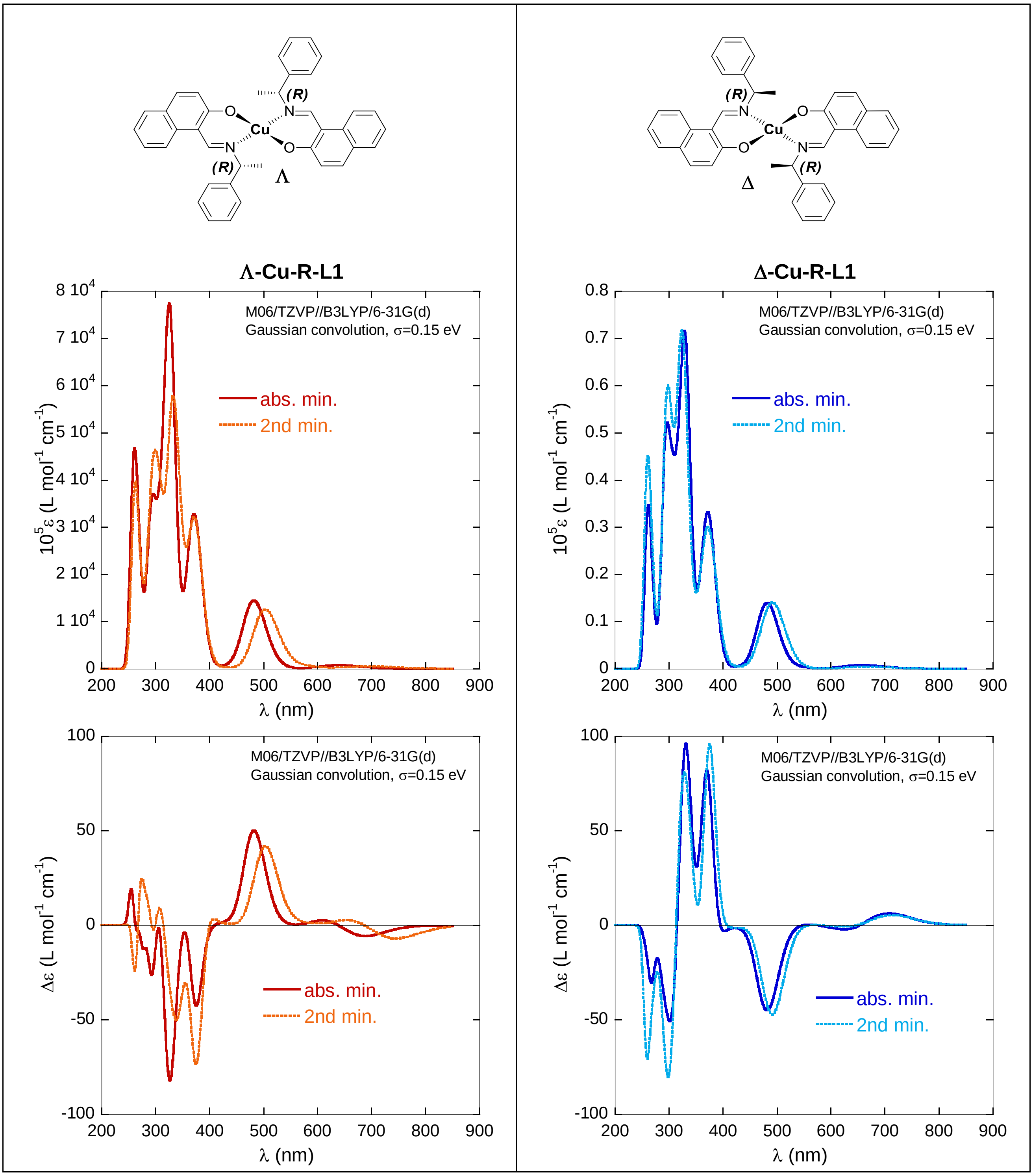


Figure S3. UV-vis and CD component spectra calculated with M06/TZVP//B3LYP/6-31G(d) on low-energy structures of **Λ**-(*R*,*R*)-complex (left) and **Δ**-(*R*,*R*)-complex (right) **Cu-L1**.

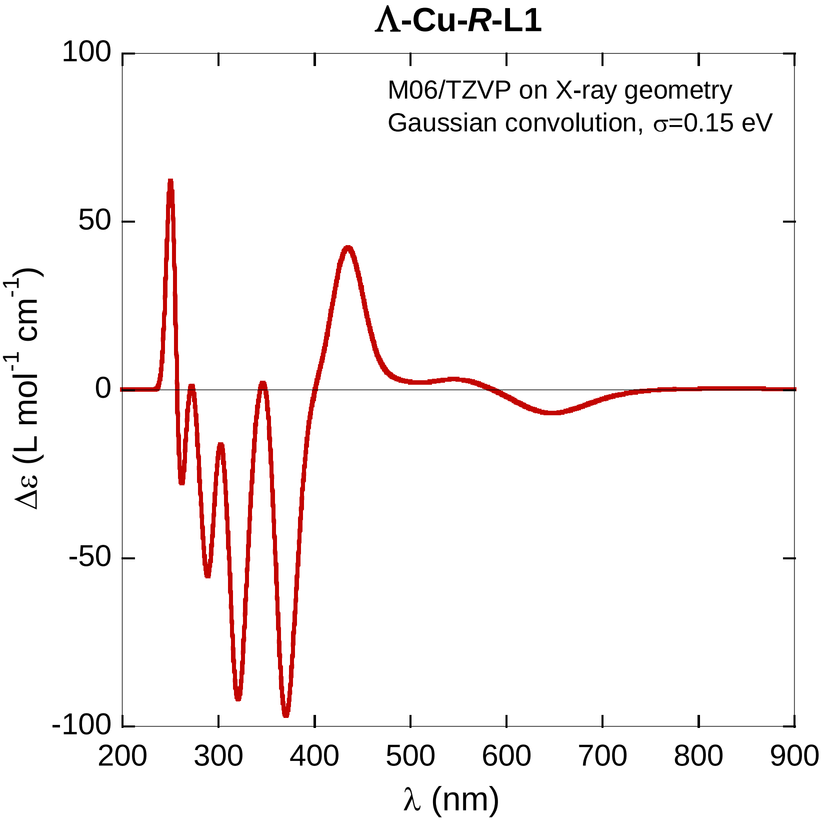


Figure S4. CD spectrum calculated with M06/TZVP on the X-ray geometry of complex **Λ-Cu-*R*-L1** after optimization of the hydrogen atoms only at B3LYP/6-31G(d) level.

Table S4. M06/TZVP calculated transition energies, oscillator strength, rotational strength and CI coefficients for the lowest energy structure of **Λ-Cu-*R*-L1** complex, B3LYP/6-31G(d) geometry.

```
Excited State   2:  2.003-A      1.8269 eV  678.65 nm  f=0.0002  R(10**-40 cgs)= -15.5710
    125B -> 160B      -0.22889
    127B -> 160B       0.15670
    128B -> 160B      -0.13875
    130B -> 160B       0.10755
    132B -> 160B      -0.19516
    133B -> 160B       0.18254
    135B -> 160B       0.35947
    139B -> 160B       0.15746
    142B -> 160B       0.36515
    144B -> 160B      -0.26899
    148B -> 160B       0.61868
    154B -> 160B      -0.10483

 Excited State   3:  2.003-A      1.9396 eV  639.24 nm  f=0.0041  R(10**-40 cgs)= 2.9979
    121B -> 160B       0.10430
    122B -> 160B       0.13570
    126B -> 160B      -0.10912
    129B -> 160B      -0.22250
    137B -> 160B      -0.22860
    138B -> 160B       0.24093
    141B -> 160B       0.19471
    142B -> 160B       0.10339
    143B -> 160B       0.46599
    145B -> 160B      -0.18034
    147B -> 160B       0.54271
    151B -> 160B      -0.21800
    155B -> 160B      -0.18148
    156B -> 160B      -0.16016
    157B -> 160B       0.18964

 Excited State   4:  2.003-A      1.9867 eV  624.07 nm  f=0.0001  R(10**-40 cgs)= 4.1710
    132B -> 160B       0.13658
    133B -> 160B       0.26862
    139B -> 160B       0.43139
    142B -> 160B       0.37484
    143B -> 160B      -0.10069
    144B -> 160B       0.45747
    146B -> 160B       0.44065
    148B -> 160B      -0.13274
    149B -> 160B       0.12670
    156B -> 160B      -0.18687
    157B -> 160B      -0.16390

 Excited State   8:  2.122-A      2.5730 eV  481.86 nm  f=0.0817  R(10**-40 cgs)= 119.3114
    124B -> 160B       0.10187
    126B -> 160B       0.12096
    134B -> 160B       0.13447
    137B -> 160B       0.23445
    141B -> 160B       0.32586
    143B -> 160B       0.10960
    145B -> 160B       0.13974
    147B -> 160B       0.13650
    151B -> 160B       0.40914
    155B -> 160B       0.20630
    159B -> 160B       0.64824

 Excited State  11:  2.120-A      3.2731 eV  378.80 nm  f=0.0065  R(10**-40 cgs)= -72.5158
    159A -> 162A      -0.21764
    160A -> 161A       0.28018
    139B -> 160B       0.12374
    144B -> 160B       0.13996
    156B -> 160B       0.58036
    157B -> 160B       0.50186
    158B -> 162B      -0.12046
    159B -> 161B       0.37472

 Excited State  12:  2.115-A      3.2808 eV  377.91 nm  f=0.0617  R(10**-40 cgs)= 129.3804
    159A -> 161A      -0.28493
    160A -> 161A      -0.10123
    160A -> 162A       0.29087
    145B -> 160B       0.17108
    147B -> 160B      -0.14443
    151B -> 160B      -0.13791
    156B -> 160B      -0.39644
    157B -> 160B       0.53587
    158B -> 161B      -0.16883
    159B -> 162B       0.42740

 Excited State  13:  2.130-A      3.3272 eV  372.63 nm  f=0.0159  R(10**-40 cgs)= -226.5883
    159A -> 162A      -0.25438
    159A -> 163A      -0.10227
    160A -> 161A       0.47899
    160A -> 162A       0.14477
```

```
    160A -> 164A       0.11732
    156B -> 160B      -0.41676
    157B -> 160B      -0.27424
    158B -> 162B      -0.15053
    159B -> 161B       0.55504

 Excited State  14:  2.355-A      3.3735 eV  367.52 nm  f=0.0846  R(10**-40 cgs)= 112.2994
    158A -> 161A      -0.11081
    159A -> 161A      -0.25852
    159A -> 164A      -0.16655
    160A -> 162A       0.34532
    160A -> 163A       0.19355
    141B -> 160B       0.11433
    143B -> 160B       0.14418
    156B -> 160B       0.35424
    157B -> 160B      -0.42388
    158B -> 161B      -0.12955
    158B -> 164B       0.14985
    159B -> 162B       0.45604
    159B -> 163B       0.14044

 Excited State  22:  3.066-A      3.6731 eV  337.55 nm  f=0.0040  R(10**-40 cgs)= -17.9996
    158A -> 162A       0.17155
    160A -> 161A      -0.16799
    160A -> 162A      -0.11926
    158B -> 161B       0.26081
    158B -> 162B       0.78748
    159B -> 161B       0.34062
    159B -> 162B       0.24664

 Excited State  23:  2.371-A      3.7734 eV  328.57 nm  f=0.0544  R(10**-40 cgs)= -28.4521
    156A -> 161A      -0.15351
    158A -> 161A       0.57902
    158A -> 162A      -0.19677
    159A -> 161A      -0.40219
    159A -> 162A       0.17069
    160A -> 161A       0.21824
    160A -> 162A      -0.27559
    137B -> 160B       0.11510
    145B -> 160B       0.14651
    150B -> 160B      -0.16487
    151B -> 160B      -0.15572
    155B -> 160B      -0.23712
    158B -> 161B      -0.14724
    158B -> 162B       0.13307

 Excited State  24:  2.153-A      3.7868 eV  327.41 nm  f=0.2632  R(10**-40 cgs)= -58.4328
    157A -> 162A       0.11083
    158A -> 161A       0.19204
    158A -> 162A      -0.26493
    159A -> 161A      -0.24553
    159A -> 162A       0.17823
    160A -> 161A       0.10912
    160A -> 162A       0.10671
    134B -> 160B      -0.11178
    137B -> 160B      -0.23705
    141B -> 160B      -0.16865
    145B -> 160B      -0.21705
    150B -> 160B       0.33003
    151B -> 160B       0.25646
    155B -> 160B       0.51240
    157B -> 162B       0.10073
    158B -> 161B      -0.18651
    159B -> 162B       0.10933

 Excited State  25:  2.429-A      3.7960 eV  326.62 nm  f=0.0351  R(10**-40 cgs)= -12.1137
    150A -> 162A       0.10784
    156A -> 162A      -0.14197
    158A -> 161A       0.28998
    158A -> 162A       0.57995
    159A -> 161A      -0.25371
    159A -> 162A      -0.46670
    160A -> 161A      -0.17236
    160A -> 162A      -0.20725
    155B -> 160B       0.13508
    158B -> 161B      -0.14792
    158B -> 162B      -0.21789

 Excited State  26:  2.720-A      3.8540 eV  321.70 nm  f=0.0260  R(10**-40 cgs)= -8.7583
    156A -> 161A      -0.12562
    159A -> 169A      -0.12808
    159A -> 170A       0.19631
    160A -> 169A      -0.26367
    150B -> 160B      -0.14155
    151B -> 160B      -0.28875
    154B -> 160B       0.45290
    155B -> 160B       0.49567
    158B -> 169B       0.13337
    158B -> 170B      -0.18812
    159B -> 169B       0.27172
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Excited State  29:  2.362-A      3.9006 eV  317.86 nm  f=0.0633  R(10**-40 cgs)= -29.7574
   159A -> 170A        0.15398
   160A -> 169A       -0.17052
   150B -> 160B        0.13622
   151B -> 160B        0.50927
   154B -> 160B        0.47305
   155B -> 160B       -0.48256
   156B -> 161B        0.11046
   157B -> 162B        0.12500
   158B -> 170B       -0.16366
   159B -> 169B        0.18085

Excited State  30:  2.013-A      4.0316 eV  307.53 nm  f=0.1061  R(10**-40 cgs)= -35.2504
   156A -> 161A        0.43555
   156A -> 162A       -0.18528
   157A -> 161A        0.14858
   157A -> 162A        0.37141
   158A -> 161A        0.10491
   159A -> 170A        0.15193
   160A -> 169A       -0.17939
   150B -> 160B       -0.11414
   151B -> 160B       -0.20313
   156B -> 161B        0.41731
   156B -> 162B       -0.23862
   157B -> 161B        0.21514
   157B -> 162B        0.33262
   158B -> 170B        0.14335
   159B -> 169B       -0.17880

Excited State  31:  2.008-A      4.0336 eV  307.38 nm  f=0.0055  R(10**-40 cgs)= 60.2042
   156A -> 161A       -0.31202
   156A -> 162A        0.26142
   157A -> 161A        0.32151
   157A -> 162A        0.37041
   159A -> 169A        0.15779
   160A -> 170A       -0.19058
   156B -> 161B       -0.31224
   156B -> 162B        0.28513
   157B -> 161B        0.35356
   157B -> 162B        0.35720
   158B -> 169B        0.12417
   159B -> 170B       -0.16630

 Excited State  36:  2.044-A      4.2394 eV  292.46 nm  f=0.1799  R(10**-40 cgs)= -66.5246
   159A -> 164A       -0.39014
   160A -> 163A        0.55253
   150B -> 160B        0.15047
   158B -> 164B       -0.30757
   159B -> 163B       -0.53284

Excited State  37:  2.066-A      4.2441 eV  292.13 nm  f=0.0010  R(10**-40 cgs)= 18.8485
   159A -> 163A       -0.36527
   159A -> 169A        0.12134
   160A -> 164A        0.46322
   160A -> 170A       -0.11487
   148B -> 160B        0.16849
   149B -> 160B       -0.12120
   151B -> 161B       -0.12946
   158B -> 163B        0.32885
   159B -> 164B        0.55167

Excited State  38:  2.941-A      4.3661 eV  283.97 nm  f=0.0018  R(10**-40 cgs)= 17.3289
   156A -> 163A       -0.12358
   157A -> 164A       -0.10132
   159A -> 163A       -0.12707
   160A -> 164A        0.20327
   148B -> 160B       -0.15271
   148B -> 162B       -0.15624
   149B -> 160B        0.22332
   150B -> 161B        0.10174
   151B -> 161B        0.51546
   155B -> 161B        0.47628
   156B -> 163B       -0.11429
   158B -> 163B        0.10061
   159B -> 164B        0.11745
   159B -> 170B       -0.10691
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