Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.
This journal is © the Partner Organisations 2021

Electronic supplementary information (ESI)

Switching on thermal and light-induced spin crossover by desolvation of the $[Fe(3\text{-bpp})_2](XO_4)_2\cdot$solvent (X = Cl, Re) compounds

Abdelhak Djemel,[a,b] Olaf Stefanczyk,*[a,c] Cédric Desplanches,[a] Kunal Kumar,[c] Rachid Delimi,[d] Farouk Benaceur,[b] Shin-ichi Ohkoshi,[c] and Guillaume Chastanet*[a]

[a.] *CNRS, Univ. Bordeaux, Bordeaux INP, ICMCB, UMR 5026, 87 avenue du Dr. A. Schweitzer, Pessac, F-33608 (France).*

[b.] *Research Unit of Medicinal Plants (RUMP), University Pole No 02, Laghouat 3000, attached to Biotechnology Research Center (CRBt), UV 03 BP E73 Ali Mendjeli New Town, Constantine 25000 (Algeria).*

[c.] *Department of Chemistry, School of Science The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033 (Japan).*

[d.] *Badji Mokhtar University, Laboratory of Water Treatment and Valorization of Industrial Waste, BP 12, Annaba 23000 (Algeria).*

E-mail OS: olaf@chem.s.u-tokyo.ac.jp. E-mail GS: guillaume.chastanet@icmcb.cnrs.fr.

Contents

Thermogravimetry

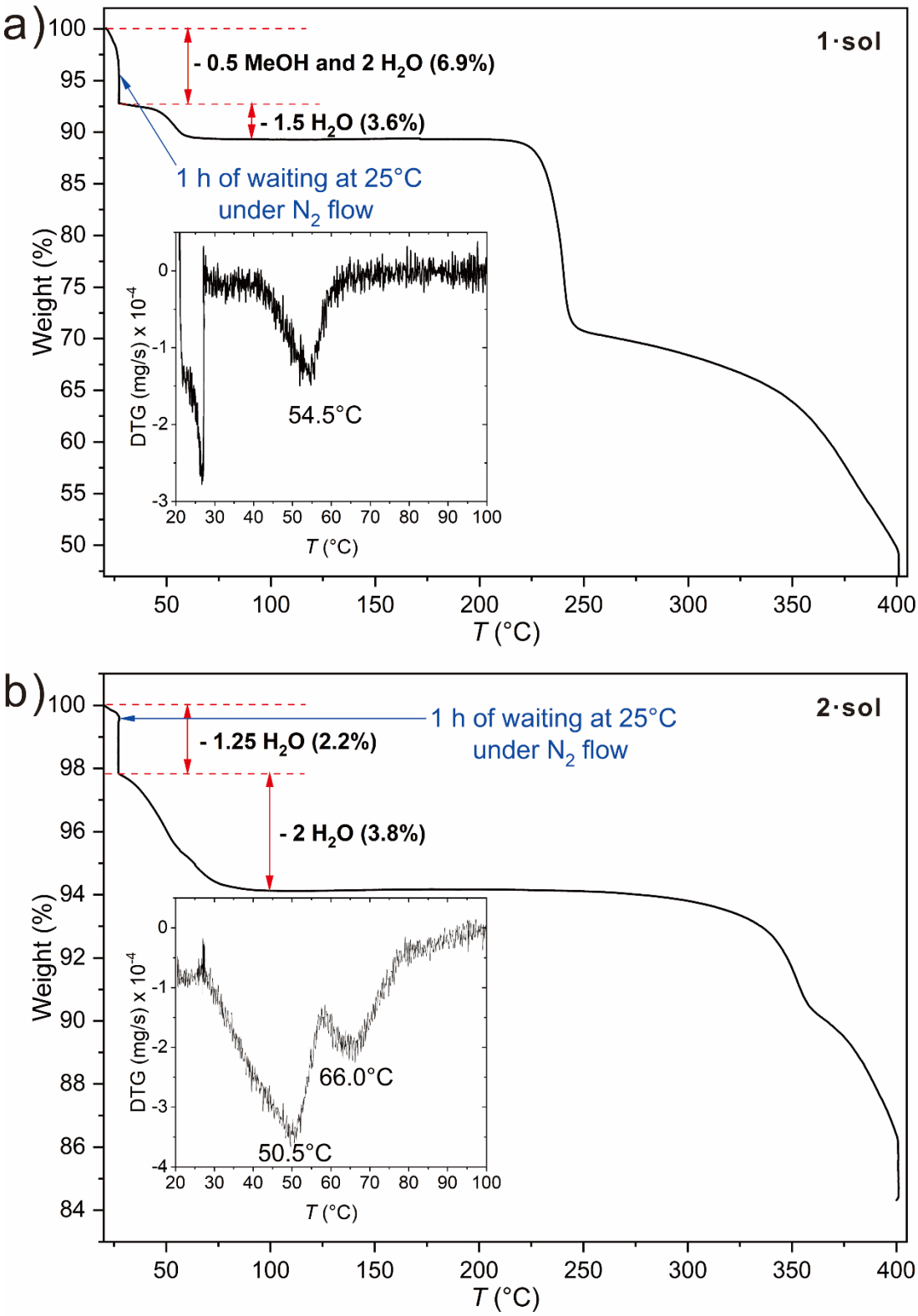

Figure S1. Thermogravimetric analyses of **1·sol** (**a**) and **2·sol** (**b**). Insets contain the first derivatives of the TGA curves (DTG).

Pictures of samples – desolvation induced colors changes

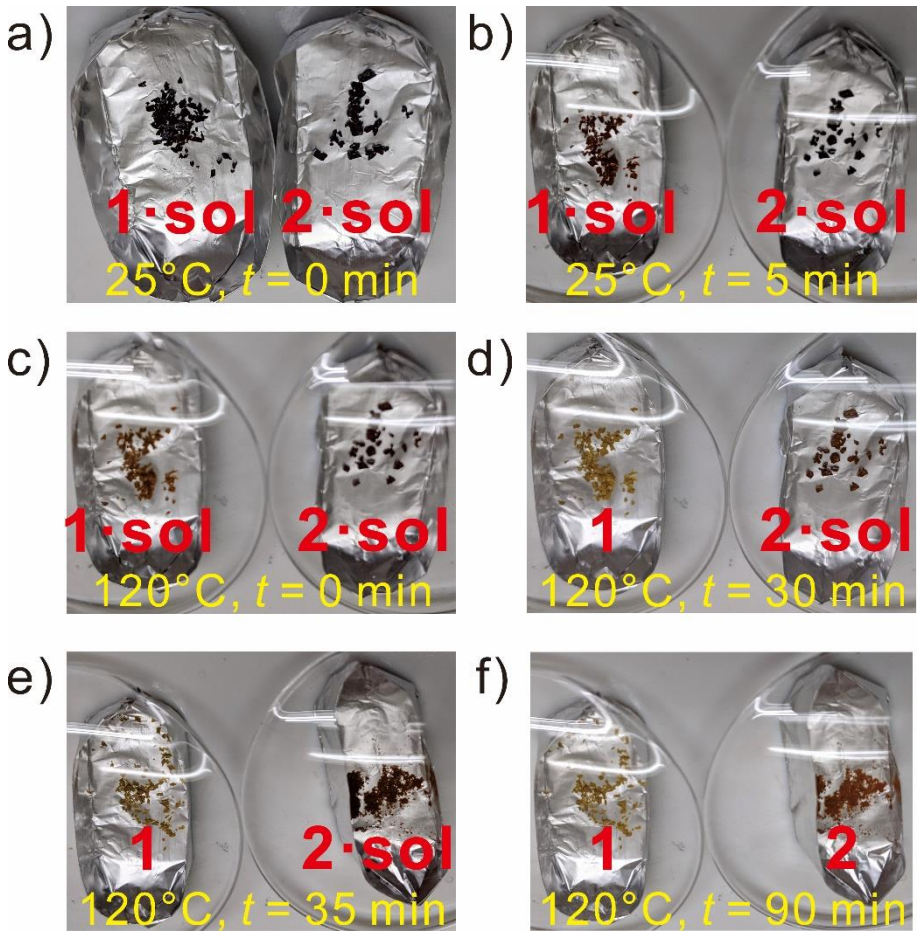

Figure S2. Pictures of **1·sol** and **2·sol** under different conditions: (**a**) freshly collected crystals, (**b**) crystallites after 5 min at 25°C, (**c**) samples just after heating to 120°C, (**d**) crystallites after 30 min at 120°C, (**e**) powdered samples for a total of 35 min at 120°C, and (**f**) powdered samples for a total of 90 min at 120°C.

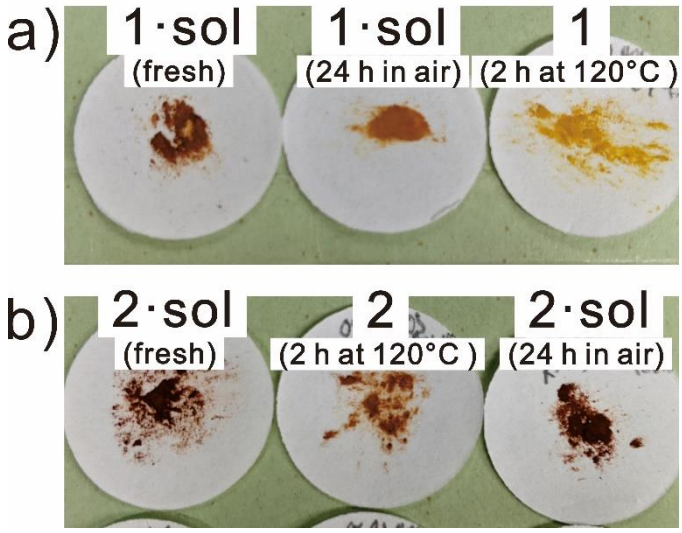

Figure S3. Room temperature pictures of **1·sol** and **2·sol** spread on cellulose paper for the fresh sample, after 24 hours in air at ambient conditions and after 2 hours of heating at 120°C.

Infrared (IR) spectroscopy

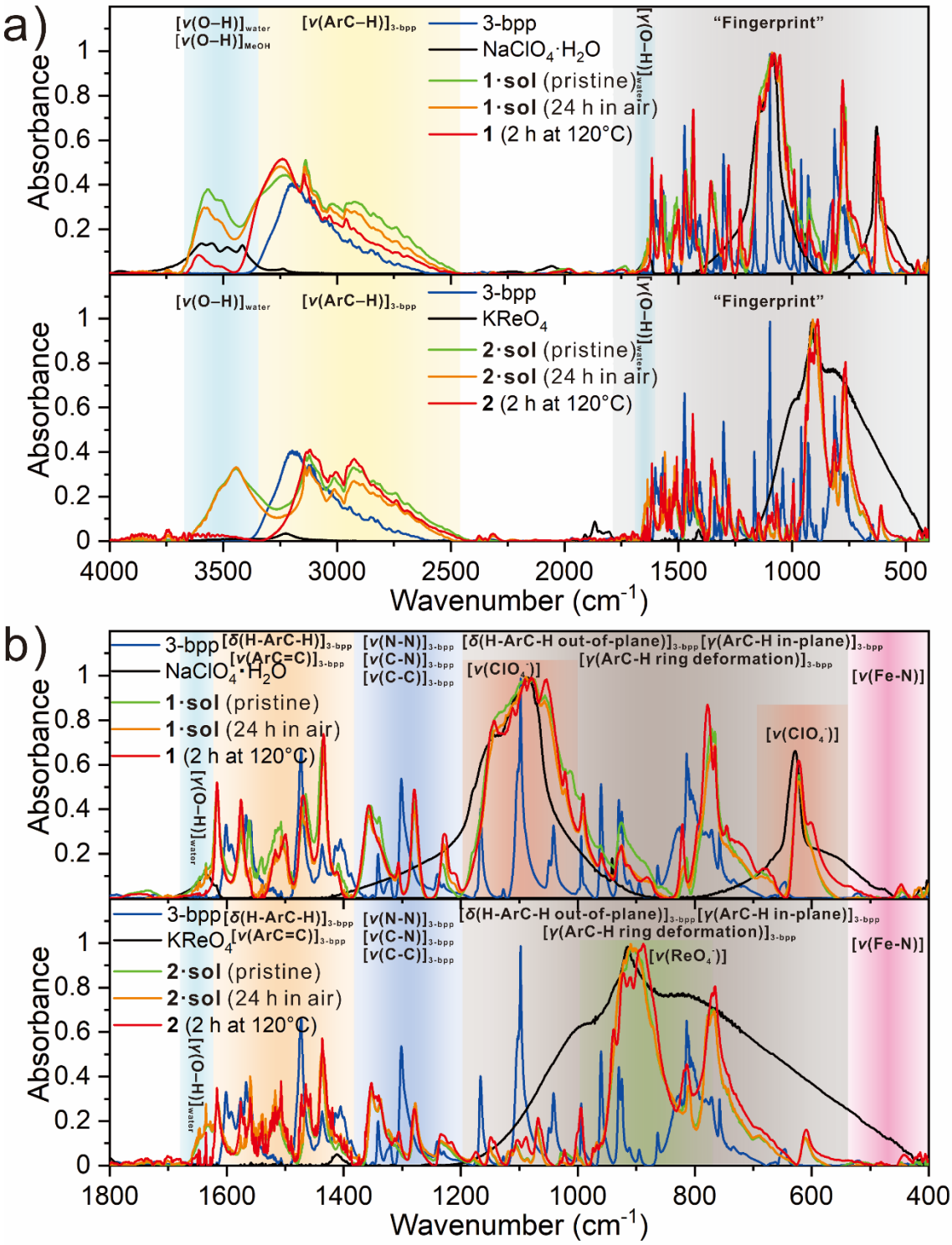

Figure S4. Infrared (IR) absorption spectra in KBr of 3-bpp, $NaClO_4 \cdot H_2O$, $KReO_4$, **1·sol** and **2·sol** (pristine, after 24 h in air at ambient conditions, and 2 h heated at 120°C) in: (**a**) the 4000 – 400 cm^{-1} range, and (**b**) the fingerprint region with assignment.

Ultraviolet-visible-near infrared (UV-vis-NIR) spectroscopy

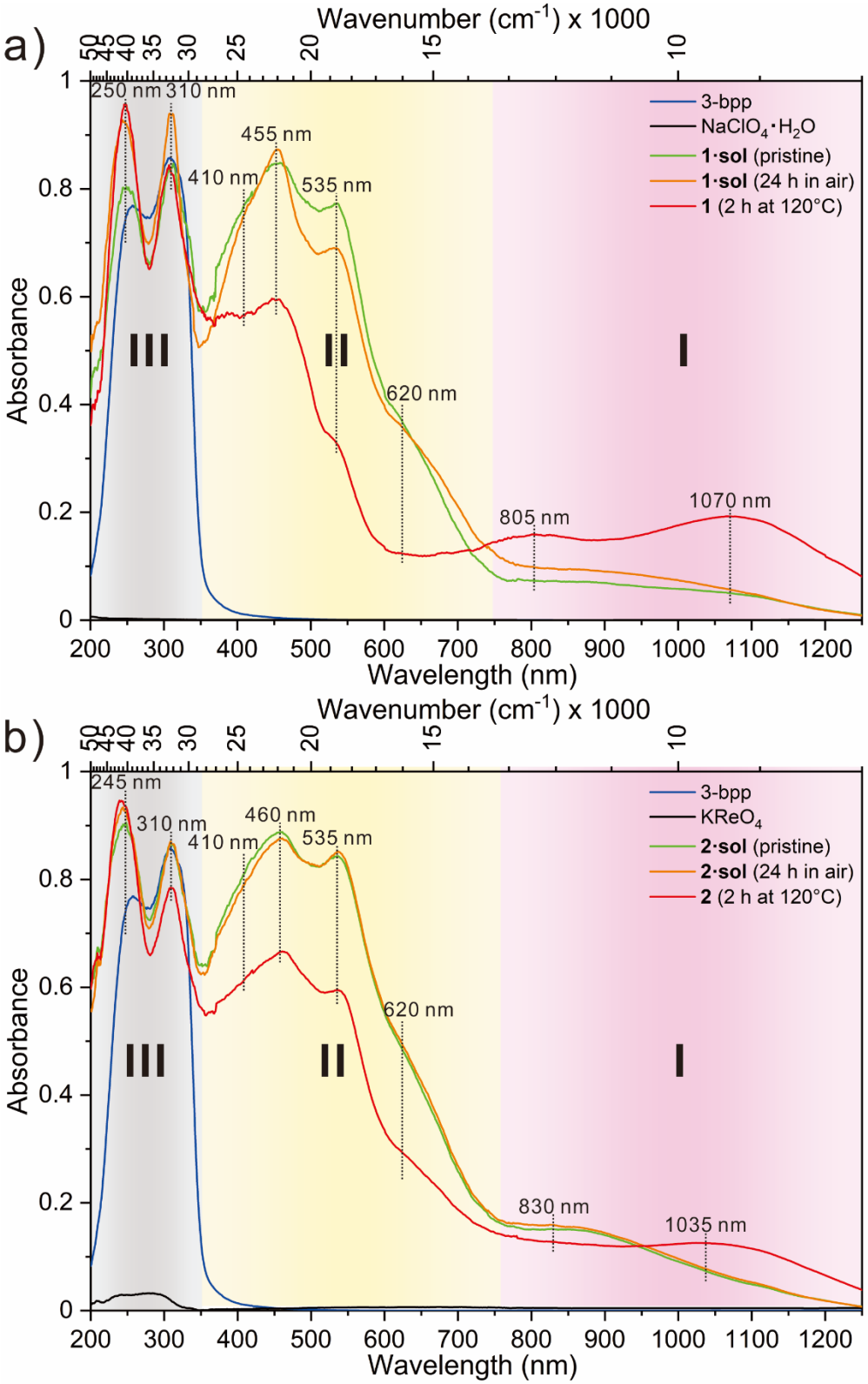

Figure S5. Room temperature solid–state UV–Vis–NIR absorption (Kubelka–Munk function) spectra with assignment of 3-bpp, $NaClO_4 \cdot H_2O$, $KReO_4$, **1·sol** (**a**) and **2·sol** (**b**) (pristine, after 24 h in dry air, and 2 h heated at 120°C) dispersed in $BaSO_4$.

Computational details

Quantum chemical calculations were done using Gaussian 16 software.[R1] Input files were prepared based on the crystal structure of **1·sol** (90 K) and **2·sol** (250 K), and $[Fe(3\text{-bpp})_2][Au(CN)_2]_2\cdot 2H_2O$ (440 K)[R2] by removing the solvents and anions forming model **A**, **B** and **C** (**Figure S6**). The single point DFT and TD-DFT calculations were performed with B3LYP functionals, using Karlsruhe type def2-SVP basis set for *C*, *N* and *H* atoms and triple-zeta def2-TZVP basis set for Fe(II) center.[R3,R4] The calculation yielded model **A** and **B** with low spin (LS) configuration with similar UV-Vis-NIR spectra (**Figure S7**) and molecular orbitals (**Figure S8**), and model **C** with complete high spin (HS) configuration (**Figure S9**). Ground state to lowest 100 electronic excited states were calculated with oscillator strength magnetic moment and constituting molecular orbitals. The molecular arrangements for relevant excited levels are presented below for all three models.

References

R1. Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

R2. A. Djemel, O. Stefanczyk, M. Marchivie, E. Trzop, E. Collet, C. Desplanches, R. Delimi and G. Chastanet, Solvatomorphism-Induced 45 K Hysteresis Width in a Spin-Crossover Mononuclear Compound, *Chem. Eur. J.*, 2018, **24**, 14760-14767.

R3. F. Weigend and R. Ahlrichs, Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297-3305.

R4. A. Schaefer, C. Huber and R. Ahlrichs, Fully optimized contracted Gaussian basis sets of triple zeta valence quality for atoms Li to Kr, *J. Chem. Phys.*, 1994, **100**, 5829.

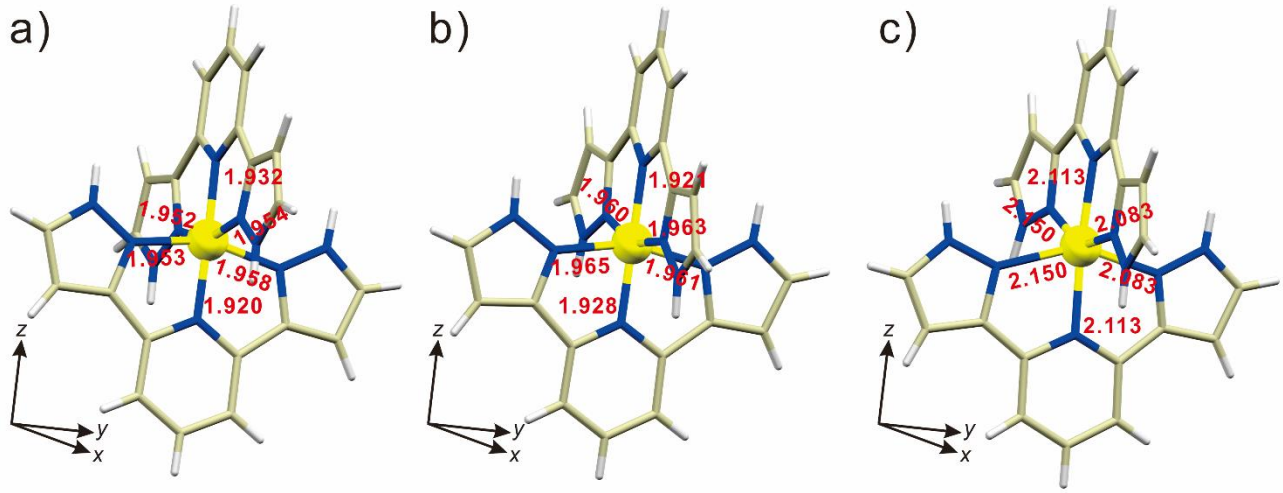

Figure S6. Models of **A** (**a**), **B** (**b**) and **C** (**c**) used for quantum chemical calculations. Legend: *C* – grey, Fe – yellow, H – white, and N – blue. Red numbers indicate bond lengths in the first coordination sphere of Fe(II) center.

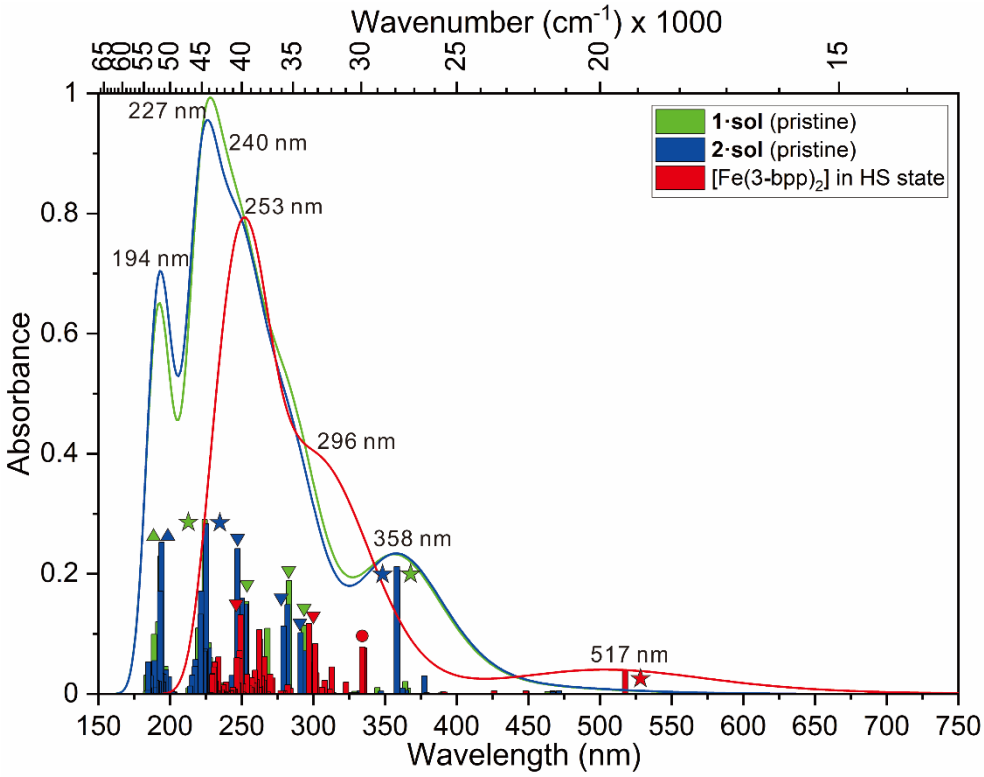

Figure S7. Calculated UV-vis spectra of **1·sol** (green), **2·sol** (blue), and $[Fe(3\text{-}bpp)_2][Au(CN)_2]_2 \cdot 2H_2O$ (red) base on models **A**, **B** and **C**, respectively. Bars indicate relative probability of electronic transitions. Symbols indicate electronic transitions with the largest contributions of: the *d-d* transitions and metal-to-ligand charge transfer (MLCT) - stars, ligand-to-ligand charge transfer (LLCT) – circles, MLCT and LLCT – down triangle, and ligand-to-metal charge transfer (LMCT).

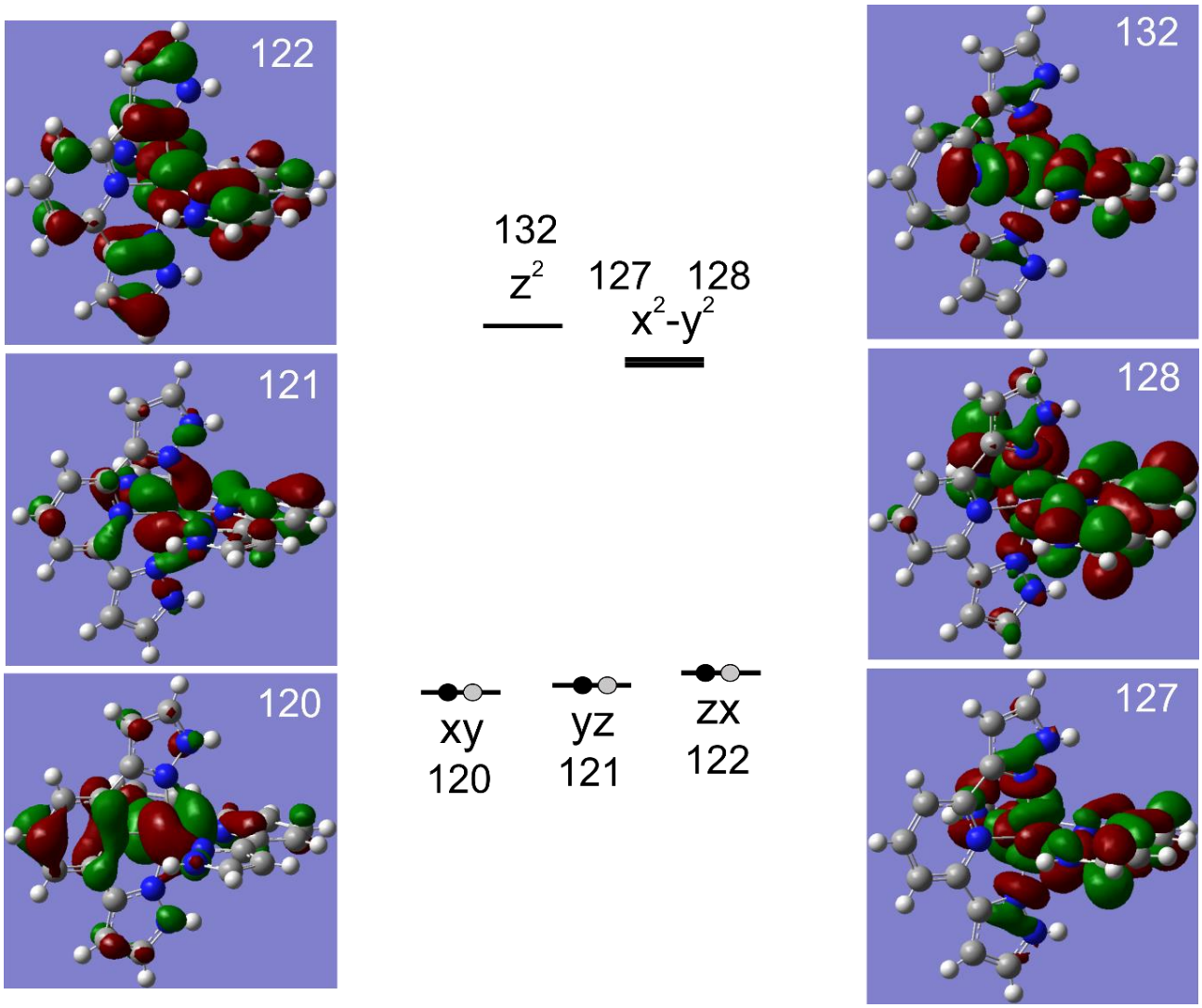

Figure S8. The energy level diagram with Fe *d*-based representative low spin molecular orbitals calculated for **1·sol** and **2·sol.**

List of excited state calculated for LS Fe(II)-based model **A** taken from complex **1·sol**.

```
Excited State   1:      Singlet-A      2.2226 eV  557.84 nm  f=0.0001  <S**2>=0.000
    112 ->127        0.15102
    118 ->127       -0.10202
    122 ->127        0.62113
    122 ->129        0.19782
    122 ->131       -0.10801
 Excited State   2:      Singlet-A      2.6554 eV  466.92 nm  f=0.0037  <S**2>=0.000
    120 ->127        0.27607
    120 ->130        0.22216
    122 ->123        0.58685
 Excited State   3:      Singlet-A      2.6760 eV  463.32 nm  f=0.0029  <S**2>=0.000
    121 ->127        0.33888
    121 ->129        0.14079
    121 ->130       -0.28310
    121 ->131       -0.10129
    121 ->132        0.15090
    122 ->124        0.46153
```

Excited State 4: Singlet-A 2.7541 eV 450.18 nm f=0.0003 <S**2>=0.000
120 ->127 0.28815
120 ->130 0.49727
120 ->132 -0.13549
122 ->123 -0.35553
Excited State 5: Singlet-A 2.7609 eV 449.06 nm f=0.0012 <S**2>=0.000
121 ->127 -0.19145
121 ->129 -0.10221
121 ->130 0.37577
121 ->132 -0.16184
122 ->124 0.50436
Excited State 6: Singlet-A 3.0546 eV 405.90 nm f=0.0005 <S**2>=0.000
120 ->123 0.46656
121 ->124 -0.32914
122 ->130 0.35447
122 ->132 -0.12394
Excited State 7: Singlet-A 3.1519 eV 393.36 nm f=0.0000 <S**2>=0.000
120 ->123 0.43792
121 ->124 0.53886
Excited State 8: Singlet-A 3.1753 eV 390.46 nm f=0.0027 <S**2>=0.000
120 ->124 0.27398
121 ->123 -0.27254
122 ->125 0.56797
122 ->126 0.11477
Excited State 9: Singlet-A 3.2854 eV 377.38 nm f=0.0068 <S**2>=0.000
120 ->124 -0.32133
121 ->123 -0.40088
122 ->125 -0.11361
122 ->126 0.44605
Excited State 10: Singlet-A 3.3876 eV 366.00 nm f=0.0069 <S**2>=0.000
120 ->125 0.29654
120 ->127 0.31088
120 ->129 0.12531
120 ->130 -0.22947
120 ->132 0.11678
121 ->125 0.39210
121 ->127 -0.15348
Excited State 11: Singlet-A 3.4054 eV 364.08 nm f=0.0154 <S**2>=0.000
120 ->125 0.36172
120 ->126 0.12111
120 ->127 -0.11710
121 ->125 -0.24863
121 ->126 -0.10102
121 ->127 -0.30987
121 ->130 -0.28453
122 ->126 0.19955
Excited State 12: Singlet-A 3.4583 eV 358.51 nm f=0.1549 <S**2>=0.000
120 ->124 0.35233
121 ->123 0.31032
121 ->125 0.15046
122 ->126 0.43615
Excited State 13: Singlet-A 3.5975 eV 344.64 nm f=0.0080 <S**2>=0.000
120 ->123 -0.26632
121 ->124 0.27201
122 ->126 -0.13073
122 ->130 0.51952

```
   122 ->132       -0.18656
 Excited State  14:      Singlet-A      3.7116 eV  334.04 nm  f=0.0020  <S**2>=0.000
   120 ->125        0.37352
   120 ->126       -0.19304
   120 ->127        0.13922
   121 ->125       -0.32867
   121 ->126        0.16365
   121 ->127        0.28196
   121 ->130        0.20607
 Excited State  15:      Singlet-A      3.7572 eV  329.99 nm  f=0.0016  <S**2>=0.000
   120 ->125        0.29848
   120 ->127       -0.33362
   120 ->129       -0.12790
   120 ->130        0.21560
   120 ->132       -0.12495
   121 ->125        0.34634
   121 ->127        0.13787
   121 ->130        0.12888
 Excited State  16:      Singlet-A      3.7720 eV  328.70 nm  f=0.0034  <S**2>=0.000
   118 ->123        0.11036
   119 ->123        0.11470
   120 ->125       -0.10251
   120 ->126        0.19889
   121 ->125       -0.10723
   121 ->126        0.62054
 Excited State  17:      Singlet-A      3.8240 eV  324.23 nm  f=0.0010  <S**2>=0.000
   120 ->126        0.62173
   121 ->126       -0.14373
   121 ->127        0.17501
   121 ->130        0.14680
```

List of excited state calculated for LS Fe(II)-based model **B** taken from complex **2·sol**.

```
 Excited State   1:      Singlet-A      2.1807 eV  568.56 nm  f=0.0000  <S**2>=0.000
   112 ->127        0.14573
   122 ->127        0.57693
   122 ->128        0.32367
   122 ->129       -0.11194
 Excited State   2:      Singlet-A      2.6298 eV  471.46 nm  f=0.0040  <S**2>=0.000
   120 ->127        0.25406
   120 ->128        0.13572
   120 ->132       -0.13052
   121 ->132       -0.14446
   122 ->123        0.53761
   122 ->124       -0.26630
 Excited State   3:      Singlet-A      2.6543 eV  467.11 nm  f=0.0028  <S**2>=0.000
   120 ->132       -0.20712
   121 ->127        0.30918
   121 ->128        0.18520
   121 ->132        0.21318
   122 ->123        0.24754
   122 ->124        0.41446
 Excited State   4:      Singlet-A      2.7362 eV  453.13 nm  f=0.0006  <S**2>=0.000
   120 ->127       -0.15838
   120 ->130       -0.14678
```

```
   120 ->132        0.46141
   121 ->127       -0.19564
   121 ->128       -0.10723
   122 ->123        0.35264
   122 ->124        0.19617
 Excited State   5:      Singlet-A      2.7465 eV  451.43 nm  f=0.0008  <S**2>=0.000
   120 ->127        0.21372
   120 ->128        0.11743
   121 ->130        0.14358
   121 ->132       -0.42926
   122 ->124        0.44289
Excited State   6:      Singlet-A      3.0260 eV  409.72 nm  f=0.0001  <S**2>=0.000
   120 ->123        0.45014
   121 ->123        0.17790
   121 ->124       -0.33150
   122 ->130        0.11955
   122 ->132       -0.34692
Excited State   7:      Singlet-A      3.1169 eV  397.77 nm  f=0.0000  <S**2>=0.000
   120 ->123        0.30425
   120 ->124       -0.35251
   121 ->123        0.29359
   121 ->124        0.42959
Excited State   8:      Singlet-A      3.1913 eV  388.51 nm  f=0.0012  <S**2>=0.000
   120 ->123       -0.23674
   120 ->124       -0.16867
   121 ->123        0.26729
   121 ->124       -0.12698
   122 ->125        0.56711
Excited State   9:      Singlet-A      3.2852 eV  377.41 nm  f=0.0225  <S**2>=0.000
   120 ->124        0.41406
   121 ->123        0.37345
   121 ->124        0.12040
   122 ->126        0.39435
Excited State  10:      Singlet-A      3.4002 eV  364.63 nm  f=0.0045  <S**2>=0.000
   120 ->127       -0.34556
   120 ->128       -0.19989
   120 ->132       -0.12863
   121 ->125        0.45554
   121 ->130        0.14467
   121 ->132       -0.23827
Excited State  11:      Singlet-A      3.4234 eV  362.17 nm  f=0.0076  <S**2>=0.000
   120 ->125        0.43477
   120 ->132        0.28703
   121 ->127        0.34396
   121 ->128        0.18084
   121 ->132       -0.16296
   122 ->126       -0.12676
Excited State  12:      Singlet-A      3.4606 eV  358.27 nm  f=0.1590  <S**2>=0.000
   120 ->123        0.11978
   120 ->124       -0.23843
   120 ->125        0.10090
   121 ->123       -0.25863
   121 ->124       -0.13309
   122 ->126        0.55495
Excited State  13:      Singlet-A      3.5714 eV  347.16 nm  f=0.0035  <S**2>=0.000
   120 ->123        0.25045
```

```
   120 ->124        0.11860
   121 ->124       -0.24810
   122 ->130       -0.18151
   122 ->132        0.53626
Excited State  14:      Singlet-A      3.7304 eV  332.36 nm  f=0.0040  <S**2>=0.000
   118 ->123       -0.10426
   120 ->125        0.36391
   120 ->127       -0.18305
   120 ->128       -0.11334
   120 ->132       -0.21194
   121 ->125       -0.33265
   121 ->126       -0.23969
   121 ->127       -0.20311
   121 ->128       -0.11523
Excited State  15:      Singlet-A      3.7513 eV  330.51 nm  f=0.0016  <S**2>=0.000
   120 ->125        0.34634
   120 ->127        0.22748
   120 ->128        0.12424
   121 ->125        0.37904
   121 ->127       -0.19390
   121 ->132        0.27152
Excited State  16:      Singlet-A      3.7956 eV  326.65 nm  f=0.0015  <S**2>=0.000
   120 ->125        0.10041
   120 ->126       -0.27997
   121 ->125       -0.13048
   121 ->126        0.58783
Excited State  17:      Singlet-A      3.8110 eV  325.33 nm  f=0.0015  <S**2>=0.000
   120 ->125        0.13588
   120 ->126        0.61862
   121 ->126        0.24556
```

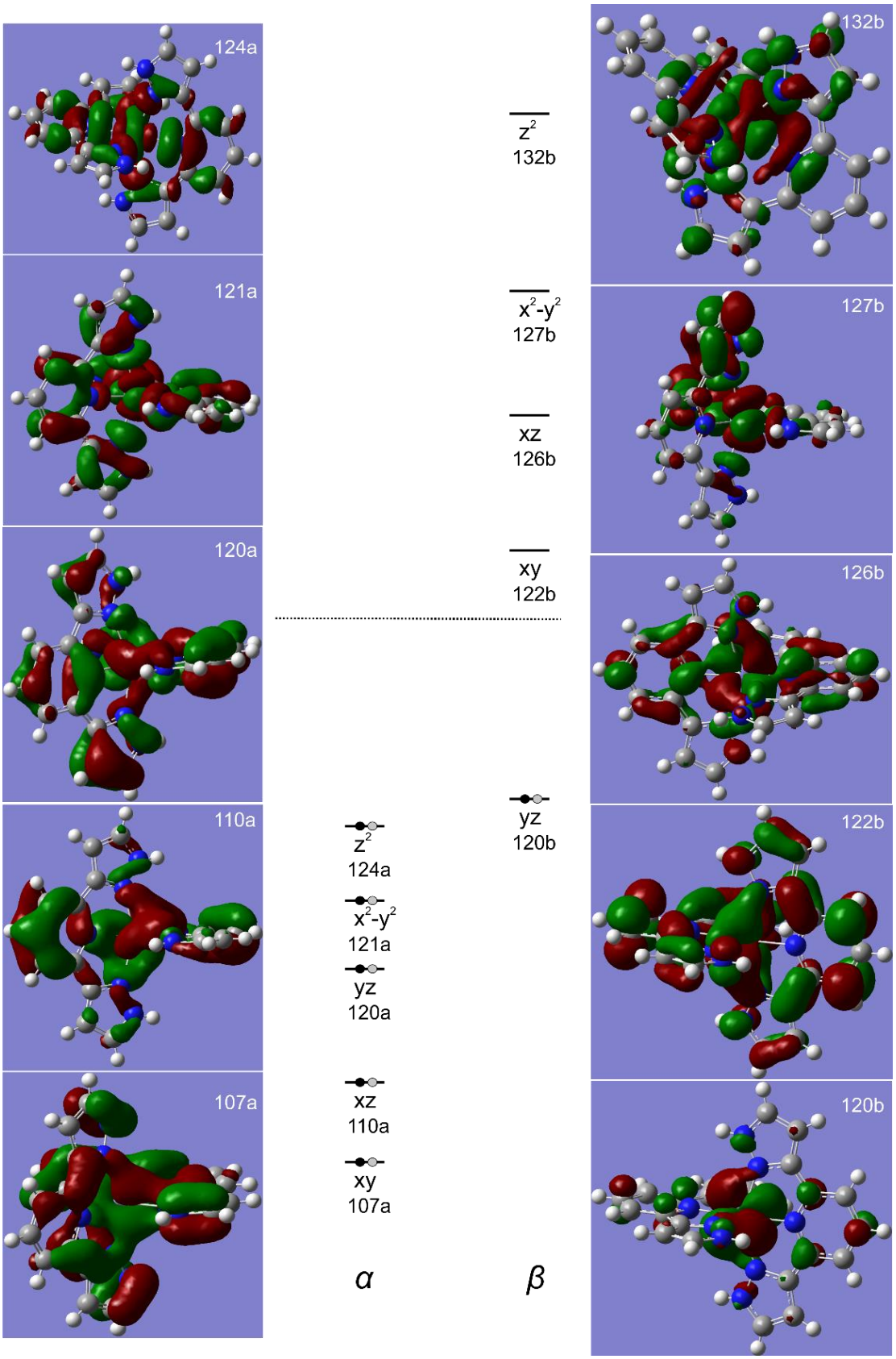

Figure S9. The energy level diagram with Fe *d*-based representative high spin molecular orbitals calculated for input file taken from reference **R2.**

List of excited state calculated for HS Fe(II)-based model **C** taken from reference **R2**.

```
Excited State   1:  5.017-A     0.1740 eV 7124.97 nm  f=0.0004  <S**2>=6.042
   120B ->121B       0.74774
   120B ->126B       0.67968
   120B <-121B       0.15524
   120B <-126B       0.15702
 Excited State   2:  5.011-A     0.2950 eV 4203.22 nm  f=0.0002  <S**2>=6.028
   120B ->122B       0.75908
   120B ->123B       0.13318
   120B ->125B       0.57158
   120B ->131B       0.16578
   120B ->132B       0.18888
 Excited State   3:  5.000-A     1.7155 eV  722.72 nm  f=0.0001  <S**2>=6.000
   120B ->127B       0.84813
   120B ->128B       0.47661
   120B ->130B      -0.15646
 Excited State   4:  5.003-A     2.1313 eV  581.72 nm  f=0.0000  <S**2>=6.007
   120B ->125B      -0.16668
   120B ->131B      -0.41475
   120B ->132B       0.81282
   120B ->133B      -0.16079
   120B ->135B      -0.29016
 Excited State   5:  5.455-A     2.3575 eV  525.91 nm  f=0.0003  <S**2>=7.188
   120A ->126A      -0.10392
   120B ->122B      -0.18688
   120B ->123B       0.95429
 Excited State   6:  5.408-A     2.3961 eV  517.45 nm  f=0.0299  <S**2>=7.062
   120B ->121B      -0.66704
   120B ->124B      -0.14861
   120B ->126B       0.70549
 Excited State   7:  5.118-A     2.6596 eV  466.17 nm  f=0.0002  <S**2>=6.300
   124A ->125A       0.97989
 Excited State   8:  5.110-A     2.6829 eV  462.12 nm  f=0.0000  <S**2>=6.279
   124A ->126A       0.96370
   124A ->127A       0.16774
 Excited State   9:  5.396-A     2.7612 eV  449.02 nm  f=0.0034  <S**2>=7.029
   120B ->122B      -0.61494
   120B ->123B      -0.12213
   120B ->125B       0.73614
   120B ->132B       0.16750
 Excited State  10:  5.397-A     2.7671 eV  448.06 nm  f=0.0040  <S**2>=7.032
   120B ->124B       0.97645
   120B ->126B       0.15656
 Excited State  11:  5.688-A     2.9102 eV  426.03 nm  f=0.0039  <S**2>=7.839
   115A ->126A      -0.13831
   116A ->125A      -0.12369
   121A ->126A       0.15024
   121A ->127A      -0.14218
   122A ->125A      -0.27309
   122A ->128A       0.31079
   123A ->126A      -0.27384
   123A ->127A       0.28160
   113B ->121B      -0.10377
   115B ->123B      -0.11020
   116B ->121B       0.13218
```

```
  118B ->121B       0.31784
  118B ->124B       0.30272
  119B ->122B       0.46728
  119B ->123B      -0.17908
  119B ->125B      -0.12489
  120B ->121B       0.10169
  120B ->126B      -0.10172
Excited State  12:  5.683-A     2.9114 eV  425.86 nm  f=0.0001  <S**2>=7.824
  115A ->125A       0.13255
  116A ->126A       0.12411
  121A ->125A      -0.15074
  121A ->128A       0.13270
  122A ->126A       0.32575
  122A ->127A      -0.28900
  123A ->125A       0.24491
  123A ->128A      -0.27338
  124A ->127A       0.14401
  115B ->121B       0.13863
  116B ->123B      -0.10254
  118B ->122B       0.39542
  118B ->123B      -0.18495
  118B ->125B      -0.11517
  119B ->121B       0.39630
  119B ->124B       0.31628
  120B ->123B      -0.12038
Excited State  13:  5.340-A     3.1102 eV  398.63 nm  f=0.0006  <S**2>=6.880
  122A ->126A      -0.17189
  122A ->127A      -0.14755
  123A ->125A      -0.17677
  123A ->128A      -0.16238
  124A ->126A      -0.16288
  124A ->127A       0.72705
  118B ->122B       0.14282
  118B ->123B       0.17216
  119B ->121B      -0.45132
  119B ->124B       0.13013
Excited State  14:  5.605-A     3.1658 eV  391.63 nm  f=0.0024  <S**2>=7.604
  121A ->126A       0.11651
  122A ->125A      -0.31560
  122A ->128A      -0.21093
  123A ->126A      -0.24440
  123A ->127A      -0.25443
  124A ->128A       0.23204
  118B ->121B       0.58741
  118B ->124B      -0.17179
  119B ->122B      -0.26724
  119B ->123B      -0.30591
Excited State  15:  5.394-A     3.1719 eV  390.89 nm  f=0.0009  <S**2>=7.024
  121A ->128A      -0.16411
  122A ->126A       0.12141
  122A ->127A       0.27260
  123A ->125A       0.13849
  123A ->128A       0.16938
  124A ->127A       0.63281
  118B ->122B      -0.25108
  118B ->123B      -0.15477
```

```
  119B ->121B       0.44897
  119B ->124B      -0.21005
Excited State  16:  5.134-A     3.2718 eV  378.95 nm  f=0.0017  <S**2>=6.339
  121A ->127A      -0.15791
  122A ->128A       0.10457
  124A ->128A       0.94909
  118B ->121B      -0.12656
  119B ->122B       0.11411
Excited State  17:  5.097-A     3.5884 eV  345.52 nm  f=0.0005  <S**2>=6.244
  121A ->125A       0.75353
  122A ->126A       0.11324
  123A ->125A       0.60398
  124A ->126A       0.11127
  119B ->121B      -0.14660
 Excited State  18:  5.083-A     3.6138 eV  343.09 nm  f=0.0002  <S**2>=6.210
  121A ->126A       0.87331
  121A ->127A       0.11538
  122A ->125A      -0.12058
  123A ->126A       0.41435
  124A ->125A       0.11309
Excited State  19:  5.228-A     3.6967 eV  335.39 nm  f=0.0574  <S**2>=6.583
  121A ->125A       0.43302
  122A ->126A      -0.41232
  122A ->127A      -0.14213
  123A ->125A      -0.27842
  118B ->123B       0.26182
  119B ->121B       0.62326
  119B ->126B       0.13319
Excited State  20:  5.255-A     3.7120 eV  334.01 nm  f=0.0587  <S**2>=6.654
  118A ->125A       0.10228
  122A ->125A       0.38586
  123A ->126A       0.37951
  115B ->122B      -0.10462
  116B ->124B      -0.11912
  118B ->121B       0.70500
  118B ->126B       0.10910
  119B ->123B       0.27478
```

Single crystal X-ray diffraction (SCXRD) studies

Table S1. Selected crystallographic parameters for **1·sol** and **2·sol**.

	1·sol	**2·sol**
Formula	$C_{22.5}H_{20}Cl_2FeN_{10}O_{11}$	$C_{22}H_{24}FeN_{10}O_{11}Re_2$
M_W (g/mol)	733.23	1032.76
T (K)	90(2)	250(2)
Crystal system, space group	Triclinic, P-1	Triclinic, P-1
a (Å)	8.2930(5)	11.6404(4)
b (Å)	8.3598(6)	11.8143(4)
c (Å)	21.9377(13)	11.9919(4)
α (°)	81.870(6)	107.9610(10)
β (°)	89.641(6)	99.9260(10)
γ (°)	89.552(6)	91.0420(10)
V (Å^3)	1505.54(17)	1540.83(9)
Z	2	2
ρ_{calc} (g/cm^3)	1.617	2.226
μ (mm-1)	0.753	8.374
F(000)	746	980
Crystal size (mm^3)	0.262 × 0.174 × 0.100	0.314 × 0.120 × 0.111
Radiation	MoK_α (λ = 0.71075)	MoK_α (λ = 0.71075)
2θ range (°)	6.198 to 54.97	4.25 to 55.064
Index ranges	-10 ≤ h ≤ 9, -10 ≤ k ≤ 10, -28 ≤ l ≤ 28	-15 ≤ h ≤ 15, -15 ≤ k ≤ 14, -15 ≤ l ≤ 15
Reflections collected / unique	14694 / 6865 [R_{int} = 0.0588, R_{sigma} = 0.0812]	38720 / 7089 [R_{int} = 0.0318, R_{sigma} = 0.0264]
Refinement method	Full–matrix least–squares on F^2	Full–matrix least–squares on F^2
Data/restraints/parameters	6865/148/500	7089/0/424
GOF on F^2	1.205	1.097
R_1/wR_2 (I>2σ(I))	0.1084/0.2077	0.0357/0.0912
R_1/wR_2 (all data)	0.1339/0.2198	0.0504/0.0992
Largest diff. peak and hole (e/Å^3)	1.28/-0.94	2.15/-2.61
CCDC number		

Table S2. Selected bond lengths and angles for **1·sol** and **2·sol**.

	1·sol	**2·sol**
Bond lengths (Å)		
Fe1-N1$_{pyr}$	1.951(5)	1.959(5)
Fe1-N2$_{py}$	1.930(5)	1.920(5)
Fe1-N3$_{pyr}$	1.955(5)	1.963(5)
Fe1-N4$_{pyr}$	1.957(4)	1.961(5)
Fe1-N5$_{py}$	1.921(5)	1.928(5)
Fe1-N6$_{pyr}$	1.952(4)	1.965(5)
Fe-N$_{aver}$	**1.944(5)**	**1.949(5)**
Angles (°)		
N1$_{pyr}$-Fe1-N2$_{py}$	78.9(2)	79.4(2)
N2$_{py}$-Fe1-N3$_{pyr}$	79.4(2)	79.7(2)
N4$_{pyr}$-Fe1-N5$_{py}$	79.3(2)	79.3(2)
N5$_{py}$-Fe1-N6$_{pyr}$	79.2(2)	79.4(2)
(N$_{pyr}$-Fe-N$_{py}$)$_{aver}$	79.2(2)	79.5(2)
N1$_{pyr}$-Fe1-N4$_{pyr}$	91.79(19)	91.6(2)
N1$_{pyr}$-Fe1-N6$_{pyr}$	91.96(19)	91.3(2)
N3$_{pyr}$-Fe1-N4$_{pyr}$	92.55(19)	92.0(2)
N3$_{pyr}$-Fe1-N6$_{pyr}$	91.73(19)	92.8(2)
(N$_{pyr}$-Fe-N$_{pyr}$)$_{aver}$	92.00(19)	91.9(2)

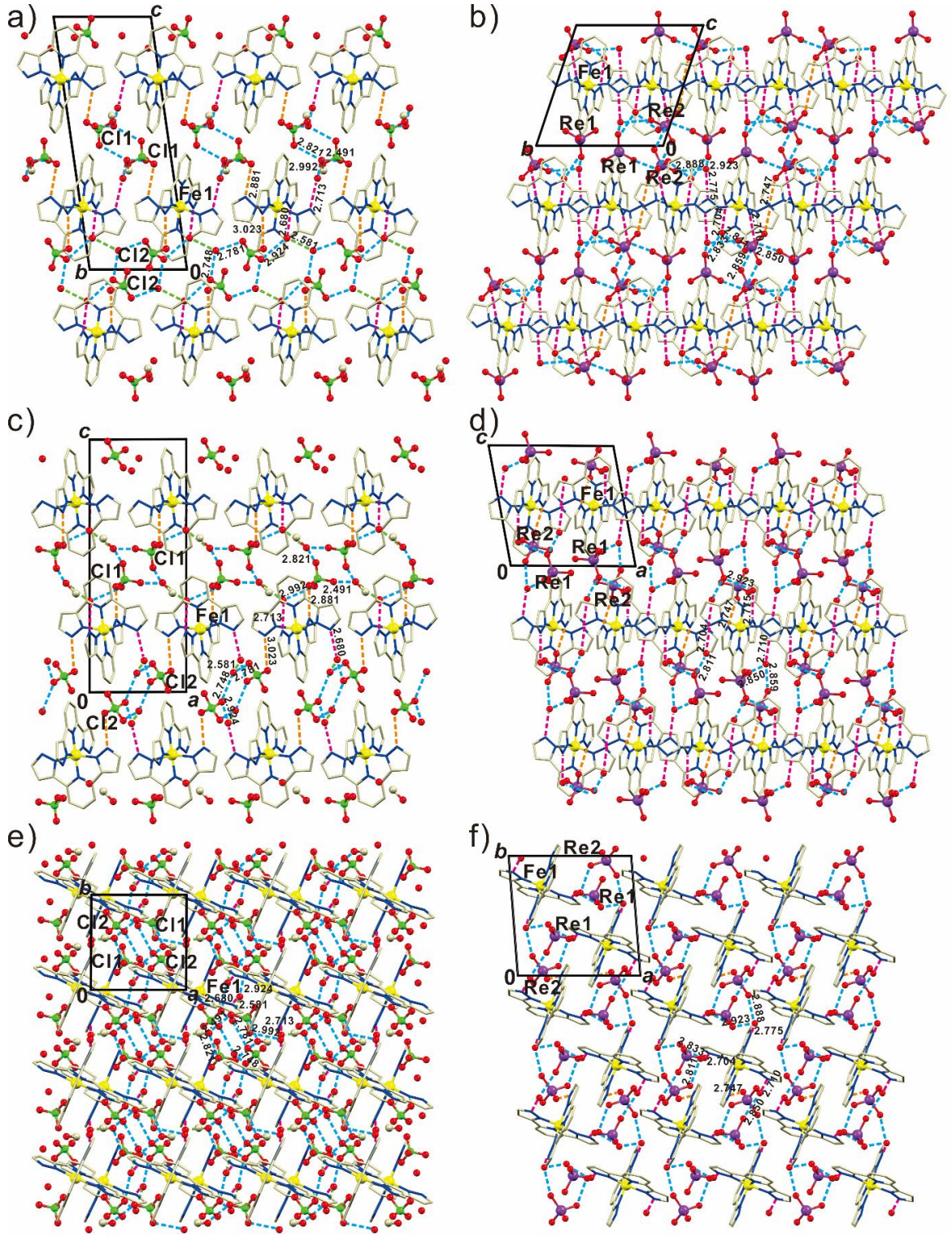

Figure S10. Packing along crystallographic directions (100) (**a** for **1·sol** and **b** for **2·sol**), (010) (**c** for **1·sol** and **d** for **2·sol**), and (001) (**e** for **1·sol** and **f** for **2·sol**) including a hydrogen bond networks between 3-bpp and XO_4^- anions (orange dashed lines), 3-bpp and water molecules (magenta dashed lines), water molecules and XO_4^- anions (blue dashed lines), and in solvent molecules (green dashed lines). The numbers correspond to the distances between the hydrogen bond donor and acceptor. For clarity, hydrogen atoms have been omitted.

Powder X-ray diffraction (PXRD) studies

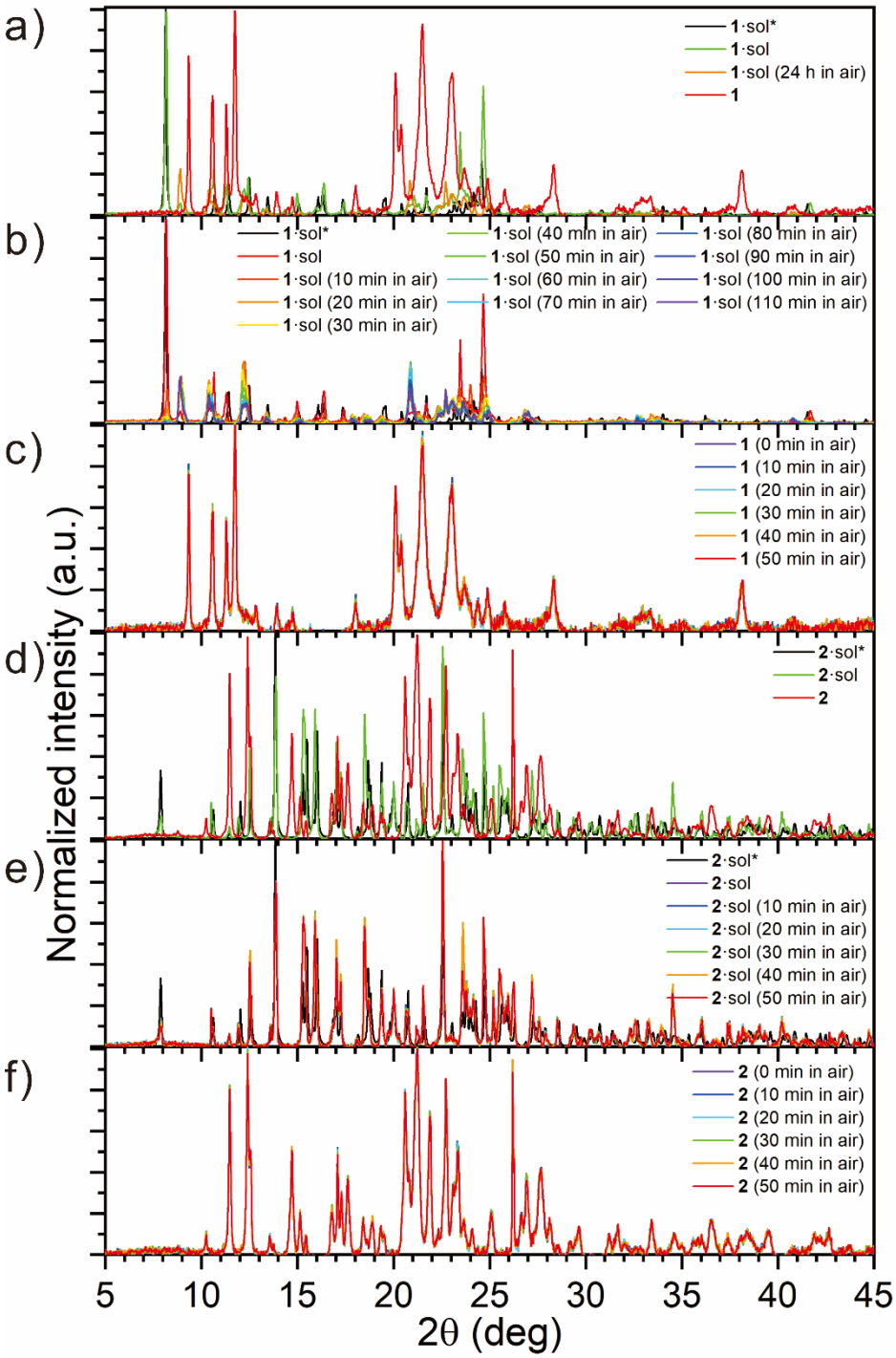

Figure S11. (**a**) Experimental PXRD patterns of **1·sol** (pristine, after 24 h in dry air, and 2 h heated at 120°C) and calculated from single-crystal X-ray diffraction data including texture effect with preferred platy orientation along (002) direction with March-Dollase parameter *M/D* = 0.6 (**1·sol***). (**b**) Time-evolution of diffractograms of pristine **1·sol**. (**c**) Time-evolution of PXRD patterns of desolvated **1** (2 h heated at 120°C). (**d**) Experimental PXRD patterns of **2·sol** (pristine and 2 h heated at 120°C) and calculated from single-crystal X-ray diffraction data (**2·sol***). (**e**) Time-evolution of diffractograms of pristine **2·sol**. (**f**) Time-evolution of PXRD patterns of desolvated **2** (2 h heated at 120°C).

Photomagnetic properties

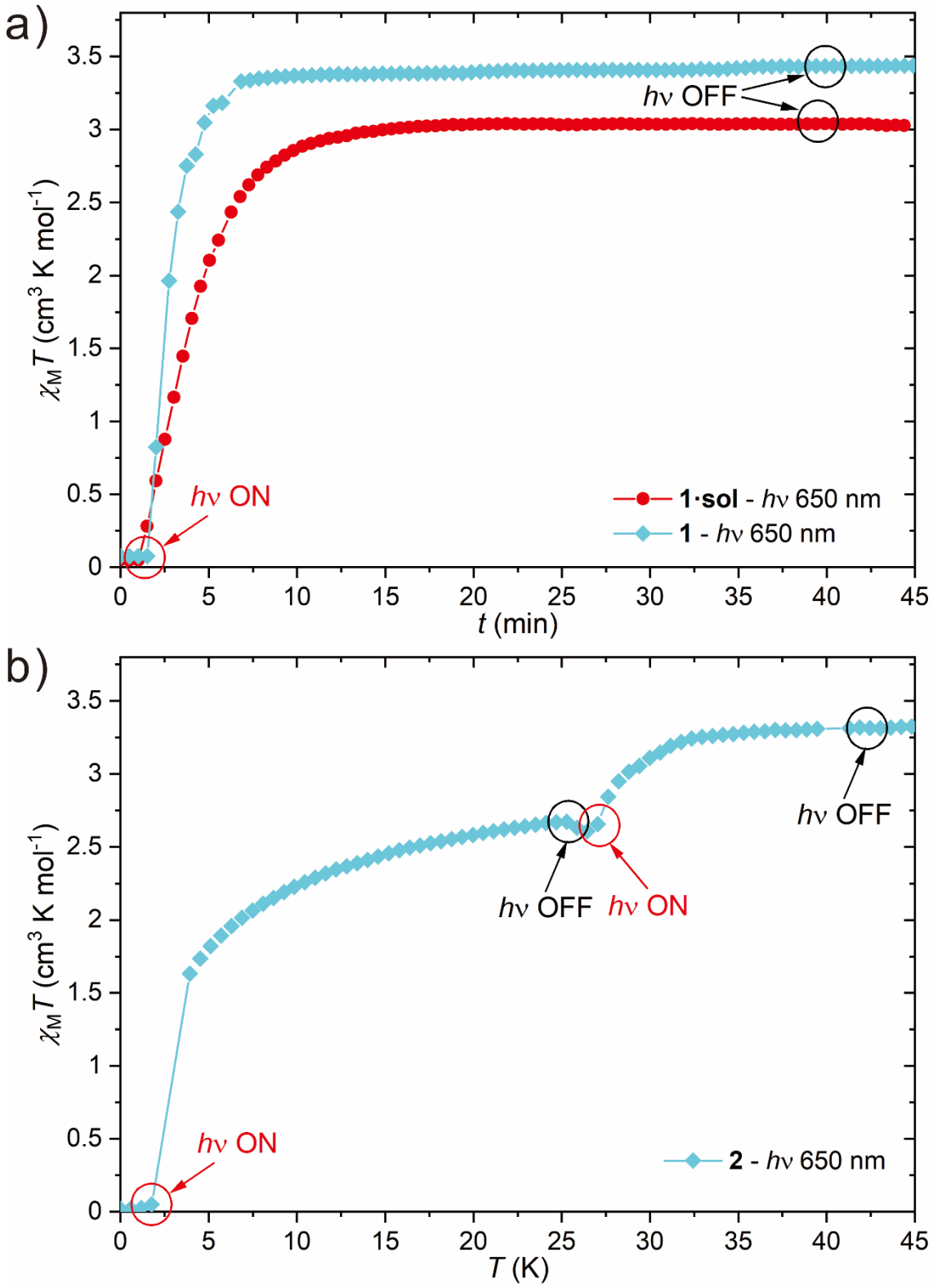

Figure S12. Time dependence of $\chi_M T$ at H_{dc} = 10 kOe during excitation at 10 K with 650 nm light (P = 5 mW/cm^2) for pristine (**1·sol**) and desolvated phases (**1** and **2**).