Supporting Information

Influence of 2-Amino-4-methylpyridine and 2-Aminopyrimidine Ligands on the Malonic Acid-Cu(II) System: Insights through Supramolecular Interactions and Photoresponse Properties

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X-ray Crystallography Study

Single crystal X-ray diffraction intensity data of were collected at 100(2) K using a Bruker APEX-II CCD diffractometer equipped with graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å). Data reduction was carried out using the program Bruker SAINT and an empirical absorption correction was applied based on multi-scan method. The structures of the title complexes were solved by direct method and refined by the full-matrix least-square technique on $|F|^2$ with anisotropic thermal parameters to describe the thermal motions of all non-hydrogen atoms using the programs (SHELXS-14$^3$) and (SHELXL-18),$^4$ respectively. All hydrogen atoms were located from difference Fourier map and refined isotropically. The summary of crystal data and relevant structure refinement parameters for (1 and 2) are given in Table S1. CCDC 1939654, 1939655 contain the supplementary crystallographic data of complex 1 and 2, respectively.

Table S1. Crystal Data and Structure Refinement Parameters for Complex 1 and 2

| Complex | 1 | 2 |
|---------|---|---|
| formula | $C_{24}H_{32}CuF_6N_6O_9P$ | $C_{22}H_{28}CuF_{12}N_{12}O_8P_2$ |
| formula weight | 757.06 | 942.04 |
| temperature (K) | 100.0 | 100 |
| wavelength (Å) | 0.71073 | 0.71073 |
| crystal system | triclinic | triclinic |
| space group | P-1 | P-1 |
| a, b, c (Å) | 9.8494(9), 10.0898(9), 17.7292(17) | 9.7997(9), 10.2097(11), 17.6484(15) |
| α, β, γ (deg) | 86.873(3), 75.394(3), 70.241(2) | 92.439(3), 98.427(2), 108.372(3) |
| volume (Å$^3$) | 1603.7(3) | 1650.2(3) |
| Z / Density (calc.) (Mg/m$^3$) | 2 / 1.568 | 2 / 1.896 |
| absorption coefficient (mm$^{-1}$) | 0.824 | 0.895 |
| F(000) | 776 | 950 |
| Crystal size[mm$^3$] | 0.28 x0.28 x0.32 | 0.3 x0.33 x0.35 |
| θ range for data collection (deg) | 2.268, 26.388 | 2.330, 26.389 |
| Limiting indices | -12<=h<=12, -12<=k<=12, -22<=l<=22 | -12<=h<=12, -11<=k<=12, -21<=l<=22 |
reflections collected/unique | 18745/ 6556 [R(int) = 0.0309] | 22537/ 6738 [R(int) = 0.0375]
completeness to θ (%) | 99.7% | 99.5%
absorption correction | multi-scan | 
max. and min transmission | 0.2602, 0.2313 | 0.2602, 0.2257
refinement method | Full-matrix least-squares on | F^2 | Full-matrix least-squares on | F^2
data/restraints/parameters | 6556 / 0 / 433 | 6738 / 0 / 514

| goodness-of-fit on F^2 | 1.048 | 1.035 |

| final R indices [I > 2σ(I)] | R_1= 0.0597, wR_2= 0.1503 | R_1= 0.0335, wR_2=0.0786 |
| R indices (all data) | R_1=0.0774, wR_2=0.1614 | R_1=0.0459, wR_2=0.0842 |

| largest diff. peak and hole (e Å^-3) | 1.889, -1.358 | 0.396, -0.393 |

R_1 = \sum|F_o|−|F_c|/\sum|F_o|, wR_2 = \left[ \sum\{w(F_o^2−|F_c|^2)^2\}/\sum\{w|F_o|^2\} \right]^{1/2}, w = 1/\{σ^2(|F_o|^2) + (aP)^2 + bP\},
where a = 0.0716 and b = 5.7633 for complex 1 and a = 0.0387 and b = 0.5600 for complex 2. P = (|F_o|^2 + 2|F_c|^2)/3 for both the structures.

Table S2. Selected Bond Distances [Å] for Complex 1 and 2

| Bonds | Distance (Å) | Bonds | Distance (Å) |
|-------|--------------|-------|--------------|
| **Complex 1** | | | |
| Cu1–O2 | 1.923(3) | Cu2–O6 | 1.966(3) |
| Cu1–O3 | 1.943(3) | Cu2–O7 | 1.926(3) |
| Cu1–O5 | 2.622(3) | Cu2–O9 | 2.504(3) |
| **Complex 2** | | | |
| Cu1–F7 | 2.4933(14) | Cu1–O6 | 1.9140(15) |
| Cu1–O2 | 1.9447(16) | Cu1–O7 | 1.9361(16) |
| Cu1–O3 | 1.9048(15) | | |

Table S3. Selected Bond Angles [°] for Complex 1 and 2

| Bond angles | Value (°) | Bond angles | Value (°) |
|-------------|-----------|-------------|-----------|
| **Complex-1** | | | |
| O2–Cu1–O3 | 93.09(12) | O6–Cu2–O7 | 91.61(12) |
| O2–Cu1–O5 | 84.41(11) | O6–Cu2–O9 | 88.90(11) |
| O2–Cu1–O2_a | 180.00 | O6–Cu2–O7_b | 88.39(12) |
| O2–Cu1–O3_a | 86.91(12) | O6–Cu2–O9_b | 91.10(11) |
| O2–Cu1–O5_a | 95.60(11) | O7–Cu2–O9 | 91.23(11) |
| O3–Cu1–O5 | 88.71(11) | O7–Cu2–O9_b | 88.77(11) |
| O3–Cu1–O5_a | 91.29(11) | | |
| **Complex-2** | | | |
| F7–Cu1–O2 | 82.40(5) | O2–Cu1–O6 | 88.17(6) |
| F7–Cu1–O3 | 88.62(6) | O2–Cu1–O7 | 172.96(6) |
| F7–Cu1–O6 | 86.53(5) | O3–Cu1–O6 | 174.39(6) |
| F7–Cu1–O7 | 104.60(5) | O3–Cu1–O7 | 85.56(6) |
| O2–Cu1–O3 | 93.97(6) | O6–Cu1–O7 | 92.95(6) |

a = 1–x,1–y,1–z; b = 2–x,–y,1–z

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Table S4. Geometrical Parameters for the Hydrogen Bonds of Complex 1 and 2

| D–H···A     | D–H [Å] | H···A [Å] | D···A [Å] | D–H···A [°] | Symmetry     |
|-------------|---------|-----------|-----------|------------|--------------|
| Complex 1   |         |           |           |            |              |
| N2–H2A···O3 | 0.8800  | 2.1700    | 3.020(5)  | 161        | –            |
| N2–H2A···O2 | 0.8800  | 2.3700    | 2.982(5)  | 127        | 1–x, 1–y, 1–z|
| N2–H2B···F6 | 0.8800  | 2.3200    | 3.088(5)  | 146        | –            |
| N3–H3···O5  | 0.8800  | 1.8400    | 2.710(5)  | 169        | –            |
| N4–H4A···O6 | 0.8800  | 2.1900    | 2.984(5)  | 150        | –            |
| N4–H4B···O1 | 0.8800  | 1.9900    | 2.849(5)  | 164        | 1–x, y, 1–z  |
| N5–H5···O7  | 0.8800  | 1.8000    | 2.673(4)  | 170        | –            |
| N6–H6A···O8 | 0.8800  | 2.0700    | 2.901(5)  | 157        | –            |
| N6–H6B···F4 | 0.8800  | 2.3300    | 3.097(5)  | 156        | 2–x, 1–y, 1–z|
| N8–H8A···O6 | 0.8700  | 1.9100    | 2.753(4)  | 162        | 2–x, –y, 1–z |
| O9–H9A···O1 | 0.8700  | 1.9900    | 2.854(4)  | 176        | 1+x, y, z    |
| C2–H2C···O8 | 0.9900  | 2.5900    | 3.279(5)  | 126        | –            |
| C5–H5A···O4 | 0.9900  | 2.3800    | 3.338(5)  | 162        | 1+x, y, z    |
| C10–H10···F1| 0.9500  | 2.4400    | 3.071(5)  | 123        | –            |
| C11–H11···F5| 0.9500  | 2.5200    | 3.459(6)  | 170        | –            |
| C18–H18C···F1| 0.9800  | 2.5400    | 3.466(6)  | 157        | 1–x, 1–y, –z |
| C20–H20···F4| 0.9500  | 2.2500    | 3.076(7)  | 144        | 2–x, 1–y, 1–z|
| C23–H23···O9| 0.9500  | 2.3800    | 3.217(6)  | 147        | 2–x, –y, 1–z |
| Complex 2   |         |           |           |            |              |
| N1–H1B···O7 | 0.8800  | 2.1200    | 2.947(2)  | 155        | –            |
| N2–H2···O7  | 0.8800  | 2.5300    | 3.255(2)  | 140        | –            |
| N2–H2···O8  | 0.8800  | 1.8700    | 2.724(2)  | 162        | –            |
| N4–H4A···N6 | 0.8800  | 2.2000    | 3.061(3)  | 167        | –x, –y, 1–z  |
| N4–H4B···O3 | 0.8800  | 2.3000    | 3.099(2)  | 151        | –            |
| N5–H5···O4  | 0.8800  | 1.7600    | 2.613(2)  | 163        | –            |
| N7–H7A···N9 | 0.8800  | 2.1900    | 3.056(3)  | 167        | 2–x, 1–y, 2–z|
| N7–H7B···F6 | 0.8800  | 2.3200    | 3.123(3)  | 152        | –            |
| N7–H7B···O6 | 0.8800  | 2.4800    | 3.148(2)  | 133        | –            |
| N8–H8A···O5 | 0.8800  | 1.8200    | 2.658(2)  | 158        | –            |
| N10–H10···O1| 0.8800  | 2.5800    | 3.172(2)  | 126        | –            |
| N10–H10···O2| 0.8800  | 1.9400    | 2.814(2)  | 175        | –            |
| N11–H11A···O6| 0.8800  | 2.1200    | 2.857(2)  | 140        | –            |
| N11–H11B···N3| 0.8800  | 2.1700    | 3.030(3)  | 167        | 1+x, 1+y, z  |
| C2–H2A···O5 | 0.9900  | 2.4700    | 3.378(3)  | 152        | x, –1+y, z   |
| C2–H2B···F1 | 0.9900  | 2.4200    | 3.228(3)  | 139        | –            |
| C5–H5A···O4 | 0.9900  | 2.5600    | 3.429(3)  | 147        | x, 1+y, z    |
| C8–H8···F9  | 0.9500  | 2.3300    | 3.224(2)  | 157        | –1+x, y, z   |
| C9–H9···F11 | 0.9500  | 2.5100    | 3.269(3)  | 137        | –1+x, y, z   |
| C10–H10A···F10| 0.9500  | 2.4400    | 3.092(3)  | 125        | –x, –y, 1–z  |
| C12–H12···O8| 0.9500  | 2.5800    | 3.467(3)  | 156        | x, –1+y, z   |
| Cg(i)···Cg(j) | Cg(i)···Cg(j) | α (°) | β (°) | γ (°) | Cg(i)–perp[Å] | Cg(j)–perp[Å] | Symmetry |
|---------------|---------------|-------|-------|-------|---------------|---------------|----------|
| Complex 1     |               |       |       |       |               |               |          |
| Cg(5)[2]···Cg(6) | 3.702(3)       | 7.52  | 18.72 | 24.90 | 3.358         | 3.507         | 2–x, –y, 1–z |
| Cg(6)[3]···Cg(5) | 3.703(3)       | 7.52  | 24.90 | 18.72 | 3.507         | 3.358         | 2–x, –y, 1–z |
| Complex 2     |               |       |       |       |               |               |          |
| Cg(3)[2]···Cg(4) | 3.9709(12)     | 7.89  | 30.94 | 30.91 | 3.407         | 3.406         | x, y, z   |
| Cg(4)[3]···Cg(3) | 3.9710(12)     | 7.89  | 30.94 | 30.94 | 3.406         | 3.407         | x, y, z   |
| Cg(5)[4]···Cg(6) | 3.7657(12)     | 6.43  | 26.82 | 27.20 | 3.349         | 3.361         | x, y, z   |
| Cg(6)[5]···Cg(5) | 3.7657(12)     | 6.43  | 27.20 | 26.82 | 3.361         | 3.349         | x, y, z   |

Cg(i) and Cg(j) denotes centroid of i\textsuperscript{th} and j\textsuperscript{th} ring respectively of complex 1: Cg(5) [N3/C7/C8/C9/C10/C11], Cg(6) [N5/C19/C20/C21/C22/C23]; Cg(i) and Cg(j) denotes centroid of i\textsuperscript{th} and j\textsuperscript{th} ring respectively of complex 2: Cg(3) [N2/C7/ N3/C10/C9/C8], Cg(4) [N5/C11/ N6/C14/C13/C12], Cg(5) [N8/C15/ N9/C18/C17/C16], Cg(6) [N10/C19/C20/C21/N12/C22]
**Solid-state UV−vis Study**

Solid-state UV−vis spectroscopy was carried out using Perkin Elmer UV−vis Lambda 365 instrument. For solid-state UV−vis spectroscopy, complex 1 and 2 were dissolved in N,N-dimethylformamide (DMF) at in right proportion (25 mg/mL) and sonicated for 15 min. Then, a thin film of each was deposited over a glass plate and dried in vacuum for 1 day. After 1 day, UV−vis spectra have been recorded.

**Device Fabrication for I−V Measurements**

Electrical characterization was performed on the synthesized complexes based metal-semiconductor (MS) junction devices. These devices were fabricated by depositing a thin film of well dispersion of synthesized complexes. To develop the thin films, ITO (Indium Tin Oxide) coated glass substrates were cleaned by acetone, ethanol and distilled water with the help of an ultra-sonicator. After that the complexes were separately mixed with N,N-dimethyl formamide (DMF) in right proportion (25 mg/mL) and sonicated for several minutes until it produces stable dispersion. Then on the top of the cleaned ITO coated substrates, stable dispersion of the just prepared complexes was spun firstly at 700 rpm for 4 min and another 6 min at 1100 rpm with the help of SCU 2700 spin coating unit. To evaporate the solvent, as-deposited thin films were annealed under vacuum at 75°C for 45 minutes. For the characterization of the developed thin film, the thickness of the active layer of the films was measured by surface profiler as ~0.9 μm. 99.99% pure Aluminium (Al) was chosen as the metal-electrode and was deposited on to the active layer to prepare the metal–semiconductor (MS) interface through shadow mask by thermal evaporation technique with the help of vacuum coating unit under a base pressure of 10⁻⁶ Torr. The effective areas of the films were maintained as 7.065 × 10⁻⁶ m².
For electrical characterization of the devices, the current-voltage (I-V) characteristic was recorded under dark and AM 1.5G radiation with the help of a Keithley 2635B source meter by two-probe technique at corresponding applied bias voltage sequentially within the limit ±2 V. All the preparation and measurements were performed at room temperature and under ambient conditions.

**Computational Details**

The $P\overline{1}$ primitive triclinic crystal structure was optimized with the density functional theory method using the CASTEP program code of Accelrys, Inc. It was relaxed with the experimental unit cell parameters fixes. The calculations were performed within the Generalized-Gradient approximation (GGA) and the Perdew-Burke-Ernzerhof (PBE) formulation for the exchange-correlation functional. Ultrasoft pseudopotentials were used in the geometric optimization of this work with the relativistic treatment of the Koelling-Harmon. A plane-wave basis set with 351 eV cut-off was applied. The k-mesh points over the Brillouin zone was generated with parameters $1 \times 1 \times 1$ the Monkhorst-Pack-scheme. The energy tolerance for self-consistent field (SCF) convergence was $2 \times 10^{-6}$ eV/atom for all calculations. The long-range dispersion correction has been included in the calculations with the Tkatchenko-Scheffler scheme. Norm-conserving pseudopotentials with a cut-off 870 eV were used for the property’s calculations. Band structures were calculated along the k-vector of the first Brillouin zone of the crystal, and Total and Partial density of states (TDOS and PDOS, respectively) were plotted concerning the Fermi level with a $3 \times 3 \times 1$ grid. The optical properties including dielectric function and optical conductivity of the crystal are calculated. Optical properties are calculated for plane polarized light with the specified polarization directions: (100) (010) (001). The smearing of 0.2 eV was employed.
**Tau (τ) parameter calculation for complex 2**

The structures with 5 coordination number can have either square pyramidal or triangular bipyramidal geometry around the metal center. In order to distinguish between these two geometries, tau (τ) parameter was proposed by Addison and co-workers.\(^{11}\) According to this, the τ parameter ranges between 0 and 1 at the extreme values giving a perfect square pyramidal and triangular bipyramidal structures, respectively. The closer the τ parameter to 0, the more similar it is to square pyramidal geometry.

\[ \tau = \frac{\beta - \alpha}{60} \] \(^{(S1)}\)

where, \(\beta\) and \(\alpha\) are, respectively, the first greatest and second greatest angles of the coordination center.

For our complex 2: \(\beta = 174.39(6)\), and \(\alpha = 172.96(6)\) (Table S3). Hence, calculated value of \(\tau = 0.024\).
Figure S1. IR plot of solid sample of complex 1 (A) after synthesis and (B) after sonicated in DMF.
Figure S2. IR plot of solid sample of complex 2 (A) after synthesis and (B) after sonicated in DMF.

In Figures S1 and S2, plot (A) represents the IR plots of the synthesized solid samples 1 and 2. The synthesized solid compounds (complexes 1 and 2) were separately dissolved in DMF (25 mg/mL) and sonicated for 15 minutes followed by evaporation of solvent DMF under vacuum (following similar procedure that we did in film formation) to get the solid mass. Plot (B) was recorded with this solid mass for both.

If DMF became coordinated to the metal complexes during the sonication, new peak should generate or peak position should shift (in comparison to that of the pure complexes 1 and 2) in IR plot. DMF shows characteristic absorption bands at 1655 and 655 cm$^{-1}$ that represent the
carbonyl bond and amide C–N bond, respectively. If DMF coordinates to the metal then the peak at 1655 cm\(^{-1}\) should shift to 1645 cm\(^{-1}\) due to the weakening of the double-bond character of the carbonyl bond, the one at 655 cm\(^{-1}\) should also shift nearly to 700 cm\(^{-1}\), possibly due to the increase in the order of the amide C–N bond. Plot B shows no characteristic peak for amide C–N bond from coordinating DMF in the IR in the range 655–700 cm\(^{-1}\) (plot (B), in Figures S1 and S2) or any shift of the peaks indicating no interaction of DMF with the complexes 1 or 2 during the chemical procedure of film formation.

Figure S3. Polymeric chain in complex 1.
Comments on the $E_g$ values of Complexes 1 and 2

It is difficult to establish exact reasons for the difference in the values of $E_g$ for complex 1 and 2. Throughout the synthesis procedure as well as during optical and electrical characterization we followed same process keeping exact experimental condition for the complexes 1 and 2. It thus appears that the changes in the $E_g$ values are due to the change in the auxiliary ligand and binding motif of malonic acid as the primary ligand. Some of the authors of this work experienced a
similar situation in recent past (ACS Omega 2018, 3, 9160–9171). We see coordination polymer offers lower $E_g$ values than supramolecular polymers, possibly due to the presence of continuous chains of covalent and coordination bonds, sometimes having conjugation, through which charge transport is facilitated. However, it is true that a proper database is required to conclude on this and we are currently underway in synthesizing similar compounds to examine their optical and electrical properties. Please see page 16 of the revised manuscript along with reference number 24 of the main text.

Figure S6. Formation of supramolecular network in complex 2.

**Electrical Characterization**

For analyzing the electrical properties, current–voltage ($I−V$) measurements of both the complexes based multiple devices has been recorded with a Keithley 2635B Sourcemeter at corresponding applied bias voltage sequentially within the limit ±2 V. Initially we have measured the $I−V$ characteristics of both the complexes (1 and 2) based multiple devices under
dark condition (Figure S7) and have calculated various major electrical parameters of those devices (Table S7).

![Figure S7. I vs. V graphs of complex 1 and complex 2 based various thin film devices in dark condition.](image)

**Table S7. Comparison Table of Electrical parameters of Complex 1 and Complex 2 based various devices in dark conditions**

| Sample  | Devices       | On/Off | Conductivity ($\times 10^{-3}$ S. m$^{-1}$) | Ideality factor | Barrier height (eV) | Series Resistance $R_S$ from $dV/d\ln I$ (Ω) | Series Resistance $R_S$ from $H$ (Ω) |
|---------|---------------|--------|-------------------------------------------|----------------|-------------------|---------------------------------------------|----------------------------------|
| Complex 1 |
| Test Device 1 | 39.45 | 1.53 | 2.23 | 0.41 | 676 | 662 |
| Test Device 2 | 32.71 | 1.05 | 2.44 | 0.44 | 705 | 703 |
| Test Device 3 | 35.68 | 1.28 | 2.65 | 0.48 | 691 | 701 |
| Test Device 4 | 30.53 | 0.98 | 2.71 | 0.49 | 711 | 704 |
| Complex 2 |
| Test Device 1 | 30.23 | 0.88 | 2.89 | 0.46 | 715 | 693 |
| Test Device 2 | 22.67 | 0.78 | 3.22 | 0.51 | 792 | 765 |
| Test Device 3 | 28.51 | 0.83 | 3.14 | 0.49 | 745 | 751 |
| Test Device 4 | 25.48 | 0.81 | 3.19 | 0.52 | 787 | 753 |
Figure S8. (A) $dV/d\ln I$ vs. $I$ and (B) $H$ vs. $I$ curve under dark and illumination condition for the complexes (1 and 2) based thin film device.

Figure S9. Capacitance vs. frequency graph of (A) complex 1 and (B) complex 2.

Table S8. Comparison Table Showing Electrical Conductivity Data

| Sample Name /Formula | Electrical conductivity ($\text{S. m}^{-1}$) | Reference |
|----------------------|---------------------------------------------|-----------|
| [Cu(SCN)(4-cyanopyridine)$_2$] | $1.0 \times 10^{-11}$ | *Inorg. Chem.* **2004**, 43, 181–188. |
| Cu$_3$Br(pyrimidine-2-thione)$_2$ | $6.0 \times 10^{-6}$ | *Inorg. Chem.* **2012**, 51, 718–727. |
| [Cu$_2$(L)$_2$(μ$_{1,3}$-SCN)$_2$]$_n$ \( \text{HL}^1 = 2$-(2- | $4.13 \times 10^{-5}$ | *Cryst. Growth Des.* |
(ethylamino)ethyliminomethyl)-6-ethoxyphenol

\[ \text{[Cu}_2\text{(adc)(4-pic)}_6\text{(H}_2\text{O)}_4\text{][ClO}_4]_2 \text{H}_2\text{adc} = \text{acetylenedicarboxylic acid} \]

\[ 11.84 \times 10^{-4} \]

\textit{New J. Chem.} \textbf{2018}, \textit{42}, 8629–8637.

\[ \text{[Cu}_6\text{I}_6\text{(pyridine-4-thione)}_4 \]

\[ 2.0 \times 10^{-9} \]

\textit{Cryst. Growth Des.} \textbf{2009}, \textit{9}, 4963–4968.

\[ \text{Cu}_3\text{(HITP)}_2 \text{(HITP}=2,3,6,7,10,11\text{-hex-aiminotriphenylene)} \]

\[ 0.2 \times 10^2 \]

\textit{Angew. Chem., Int. Ed.} \textbf{2015}, \textit{54}, 4349–4352.

\[ \text{C}_{40}\text{H}_{34}\text{Cu}_2\text{N}_6\text{O}_{18} \]

\[ 4.34 \times 10^{-6} \]

\textit{ACS Omega} \textbf{2018}, \textit{3}, 9160–9171.

\[ \text{C}_{20}\text{H}_{18}\text{CuN}_2\text{O}_{10} \]

\[ 7.6 \times 10^{-6} \]

\textit{ACS Omega} \textbf{2018}, \textit{3}, 9160–9171.

Complex 1

\[ 4.83 \times 10^{-3} \]

Present work

Complex 2

\[ 2.02 \times 10^{-3} \]

Present work

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