# Mechanochemical preparations of Donor/Acceptor materials based on coronene and silver(I) pyrazolate metallacycles.

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## Supporting information

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**NMR studies**

**Table S1.** A selection of $^1$H NMR chemical shifts of adducts **1-3** and of the starting compounds. $\Delta_{ppm}$ is the difference of the chemical shift of the hydrogen $C_4$-H of the pyrazole of the CTC upon stacking with the Coronene (third column) and of the terminal hydrogen of coronene upon stacking with the CTC (last column). Data are relative to $^1$H NMR spectra acquired in DMSO[a] or $CD_2Cl_2$[b].

| **Compounds** | **$^1$H NMR CTCs $C_4$-H resonance (ppm)** | **$\Delta_{ppm}$ CTCs $C_4$-H resonance (ppm)** | **$^1$H NMR Coronene C-H resonance (ppm)** | **$\Delta_{ppm}$ Coronene C-H resonance (ppm)** |
|---|---|---|---|---|
| Coronene | - | - | 9.10[a]; 8.98[b] | - |
| $[pz^{CF3}Ag]_3$ | 7.20[a] | - | - | - |
| $[pz^{NO2}Ag]_3$ | 7.56[a] | - | - | - |
| $[pz^{CF3}Cu]_3$ | 7.07[b] | - | - | - |
| $\{[3,5\text{-}(CF_3)_2pz]Ag\}_3$@Coronene (**1**) | 7.10[a] | -0.10 | 9.10[a] | 0 |
| $\{[3,5\text{-}(NO_2)_2pz]Ag\}_3$@Coronene (**2**) | 7.40[a] | -0.16 | 9.10[a] | 0 |
| $\{[3,5\text{-}(CF_3)_2pz]Cu\}_3$@Coronene (**3**) | 7.04[b] | -0.03 | 8.95[b] | -0.03 |

**IR spectroscopy studies**

**Table S2**. Main IR absorptions for adducts **1-3** and relative vibrational modes; notes on the redshifts or blueshifts, on comparison with the absorptions of the coronene and the corresponding starting CTC.

| {[3,5-$(CF_3)_2$pz]Ag}$_3$ @ Coronene ($cm^{-1}$) (**1**) | Coronene ($cm^{-1}$) | {[3,5-$(CF_3)_2$pz]Ag}$_3$ ($cm^{-1}$) | Main Vibrational mode | Reference | notes |
|---|---|---|---|---|---|
| 3149 | | 3153 | $C_4$-H stretching | [1] | REDSHIFT |
| 3063 | 3047 | | Aromatic C-H stretching | [2] | BLUESHIFT |
| 3028 | 3018 | | | [2] | BLUESHIFT |
| 1619 | 1615 | | Aromatic C-C stretching | [2] | BLUESHIFT |
| 1610 | 1607 | | Aromatic C-C stretching | [2] | BLUESHIFT |
| 1501 | | 1505 | Aromatic C=N stretching | [1] | REDSHIFT |
| 1315 | 1312 | | Aromatic C-C stretching | [2] | BLUESHIFT |
| 1126 | | 1143 | C-F stretching | [3] | REDSHIFT |
| 861 | 847 | | In-plane C-H bending | [2] | BLUESHIFT |

| {[3,5-$(CF_3)_2$pz]Cu}$_3$ @ Coronene ($cm^{-1}$) (**3**) | Coronene ($cm^{-1}$) | {[3,5-$(CF_3)_2$pz]Ag}$_3$ ($cm^{-1}$) | Main Vibrational mode | Reference | notes |
|---|---|---|---|---|---|
| 3149 | | 3163 | $C_4$-H stretching | [1] | REDSHIFT |
| 3061 | 3048 | | Aromatic C-H stretching | [2] | BLUESHIFT |
| 3026 | 3018 | | | [2] | BLUESHIFT |
| 1618 | 1614 | | Aromatic C-C stretching | [2] | BLUESHIFT |
| 1610 | 1607 | | | [2] | BLUESHIFT |
| 1505 | | 1508 | Aromatic C=N stretching | [1] | REDSHIFT |
| 1315 | 1312 | | Aromatic C-C stretching | [2] | BLUESHIFT |
| 1123 | | 1126 | C-F stretching | [3] | REDSHIFT |
| 968 | 957 | | C-H bending | [2] | BLUESHIFT |
| 861 | 847 | | In-planes C-H bending | [2] | BLUESHIFT |

**Table S3** EDX analysis of the surface of the samples treated with solventless mechanochemical grinding to*p*: Spot 1; *bottom*: Spot 2.

| Element | At. No. | Net | Mass [%] | Norm. Mass [%] | Atom [%] | abs. error [%] (1 sigma) | abs. error [%] (2 sigma) | abs. error [%] (3 sigma) |
|---|---|---|---|---|---|---|---|---|
| **Carbon** | 6 | 133944 | 88.33 | 88.33 | 91.57 | 9.34 | 18.68 | 28.02 |
| **Oxygen** | 8 | 6523 | 9.62 | 9.62 | 7.49 | 1.23 | 2.45 | 3.68 |
| **Fluorine** | 9 | 1132 | 1.16 | 1.16 | 0.76 | 0.21 | 0.42 | 0.63 |
| **Silicon** | 14 | 253 | 0.24 | 0.24 | 0.11 | 0.03 | 0.07 | 0.10 |
| **Silver** | 47 | 269 | 0.65 | 0.65 | 0.07 | 0.05 | 0.10 | 0.15 |
| | | | **Sum 100.00** | **Sum 100.00** | **Sum 100.00** | | | |
| **Element** | **At. No.** | **Net** | **Mass [%]** | **Norm. Mass [%]** | **Atom [%]** | **abs. error [%] (1 sigma)** | **abs. error [%] (2 sigma)** | **abs. error [%] (3 sigma)** |
| **Carbon** | 6 | 46475 | 26.86 | 37.51 | 59.43 | 2.96 | 5.92 | 8.88 |
| **Nitrogen** | 7 | 2383 | 3.86 | 5.39 | 7.33 | 0.57 | 1.14 | 1.71 |
| **Oxygen** | 8 | 3847 | 4.05 | 5.66 | 6.73 | 0.56 | 1.12 | 1.68 |
| **Fluorine** | 9 | 18682 | 14.79 | 20.65 | 20.69 | 1.72 | 3.44 | 5.16 |
| **Silicon** | 14 | 601 | 0.57 | 0.80 | 0.54 | 0.05 | 0.10 | 0.15 |
| **Silver** | 47 | 10382 | 21.48 | 29.99 | 5.29 | 0.81 | 1.62 | 2.42 |
| | | | **Sum 71.61** | **Sum 100.00** | **Sum 100.00** | | | |

**Table S4** EDX analysis of the surface of the samples treated with LAG (Liquid Assisted Grinding) to*p*: Spot 3; *bottom*: Spot 4.

| Element | At. No. | Net | Mass [%] | Norm. Mass [%] | Atom [%] | abs. error [%] (1 sigma) | rel. error [%] (1 sigma) |
|---|---|---|---|---|---|---|---|
| **Carbon** | 6 | 39769 | 26.21 | 32.65 | 51.65 | 2.91 | 11.10 |
| **Nitrogen** | 7 | 2463 | 3.85 | 4.80 | 6.51 | 0.57 | 14.68 |
| **Oxygen** | 8 | 8320 | 8.45 | 10.53 | 12.50 | 1.06 | 12.49 |
| **Fluorine** | 9 | 19762 | 15.98 | 19.91 | 19.91 | 1.85 | 11.58 |
| **Aluminium** | 13 | 1256 | 0.64 | 0.80 | 0.56 | 0.05 | 8.33 |
| **Silicon** | 14 | 6421 | 5.37 | 6.69 | 4.53 | 0.24 | 4.56 |
| **Silver** | 47 | 10430 | 19.77 | 24.63 | 4.34 | 0.75 | 3.77 |
| | | | **Sum 80.26** | **Sum 100.00** | **Sum 100.00** | | |
| **Element** | **At. No.** | **Net** | **Mass [%]** | **Norm. Mass [%]** | **Atom [%]** | **abs. error [%] (1 sigma)** | **rel. error [%] (1 sigma)** |
| **Carbon** | 6 | 36029 | 25.08 | 31.94 | 50.49 | 2.80 | 11.15 |
| **Nitrogen** | 7 | 2205 | 3.56 | 4.54 | 6.15 | 0.53 | 14.96 |
| **Oxygen** | 8 | 8918 | 9.29 | 11.83 | 14.04 | 1.15 | 12.39 |
| **Fluorine** | 9 | 17903 | 15.04 | 19.15 | 19.14 | 1.75 | 11.66 |
| **Aluminium** | 13 | 1450 | 0.79 | 1.01 | 0.71 | 0.06 | 7.60 |
| **Silicon** | 14 | 7190 | 6.15 | 7.83 | 5.30 | 0.28 | 4.50 |
| **Silver** | 47 | 9706 | 18.61 | 23.69 | 4.17 | 0.70 | 3.78 |
| | | | **Sum 78.53** | **Sum 100.00** | **Sum 100.00** | | |

**Figure S1.** Overlapped $^{1}H$ NMR spectra of $\{[3,5\text{-}(CF_3)_2pz]Ag\}_3$@Coronene (**1**) (blue line), $\{[3,5\text{-}(CF_3)_2pz]Ag\}_3$ (red line), and coronene (green line).

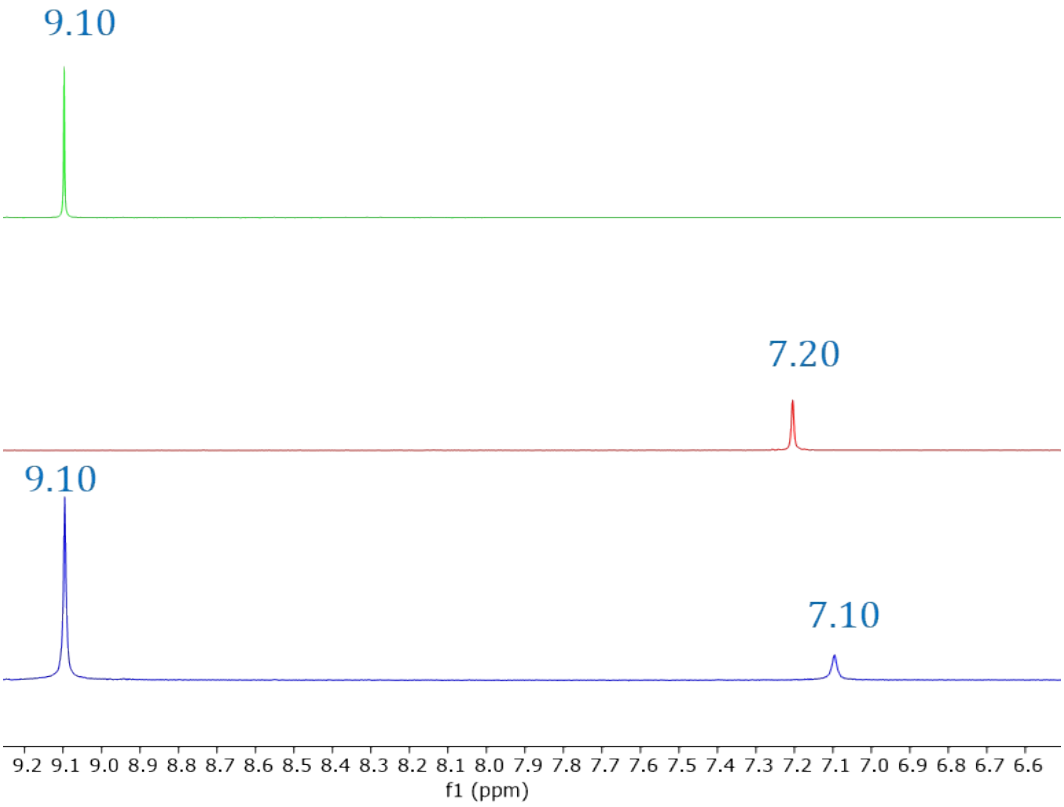


**Figure S2.** Overlapped $^{1}H$ NMR spectra of $\{[3,5\text{-}(NO_2)_2pz]Ag\}_3$@Coronene (**2**) (orange line), $\{[3,5\text{-}(NO_2)_2pz]Ag\}_3$ (blue line), and coronene (red line).

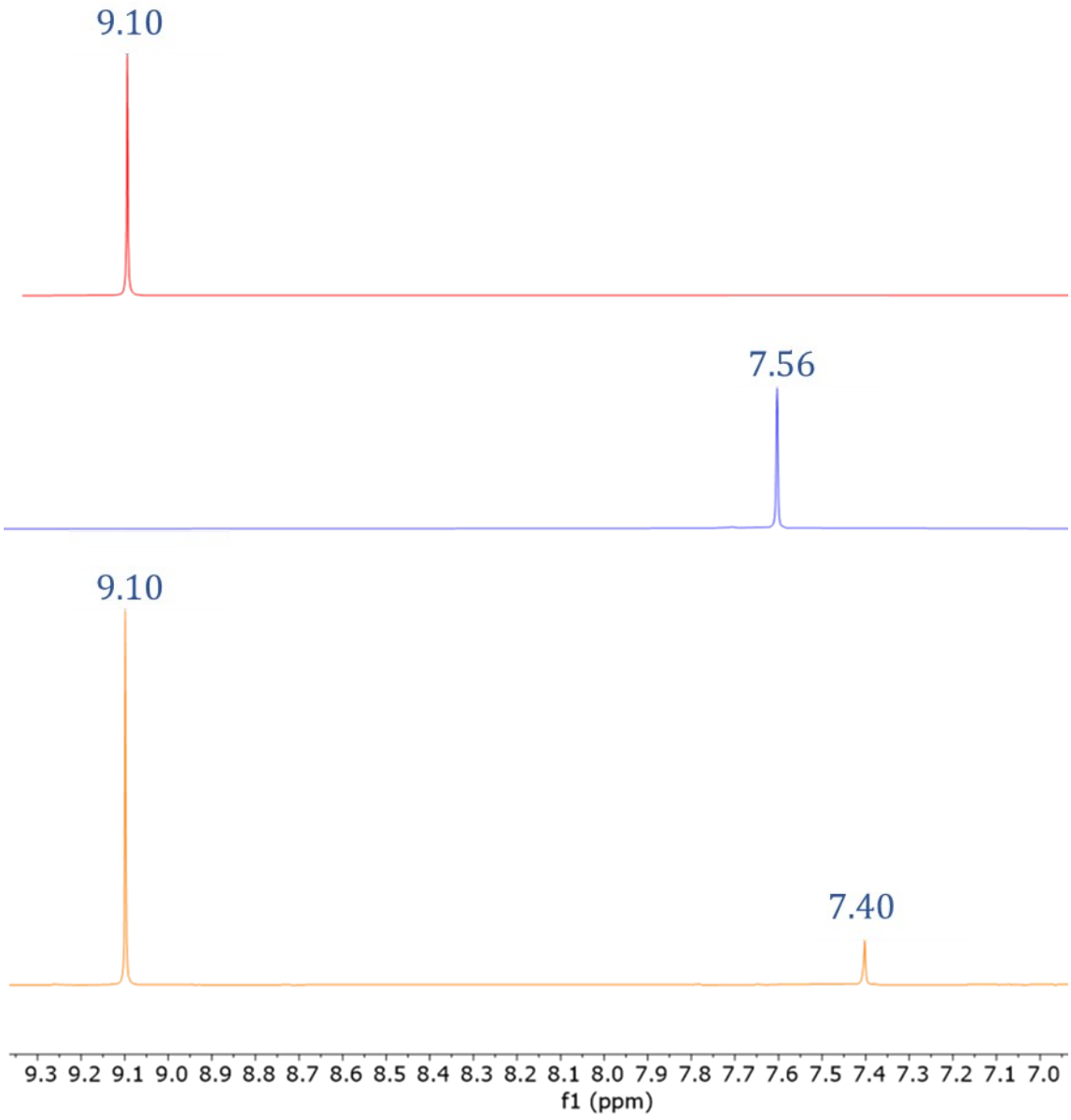


**Figure S3.** Overlapped $^{1}H$ NMR spectra of {[3,5-$(CF_3)_2$pz]Cu}$_3$@Coronene (**3**) (orange line), {[3,5-$(CF_3)_2$pz]Cu}$_3$ (blue line), and coronene (red line).

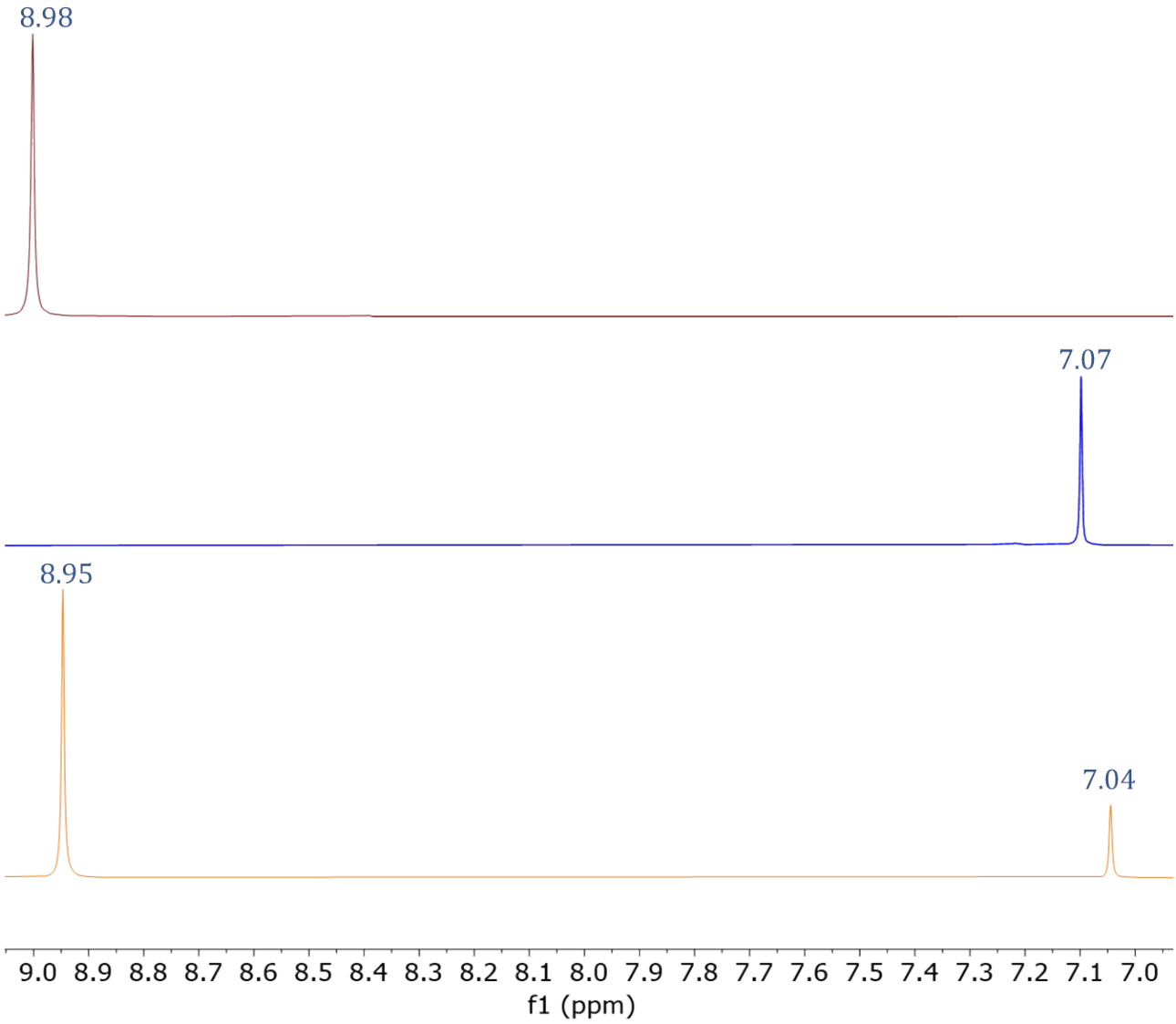
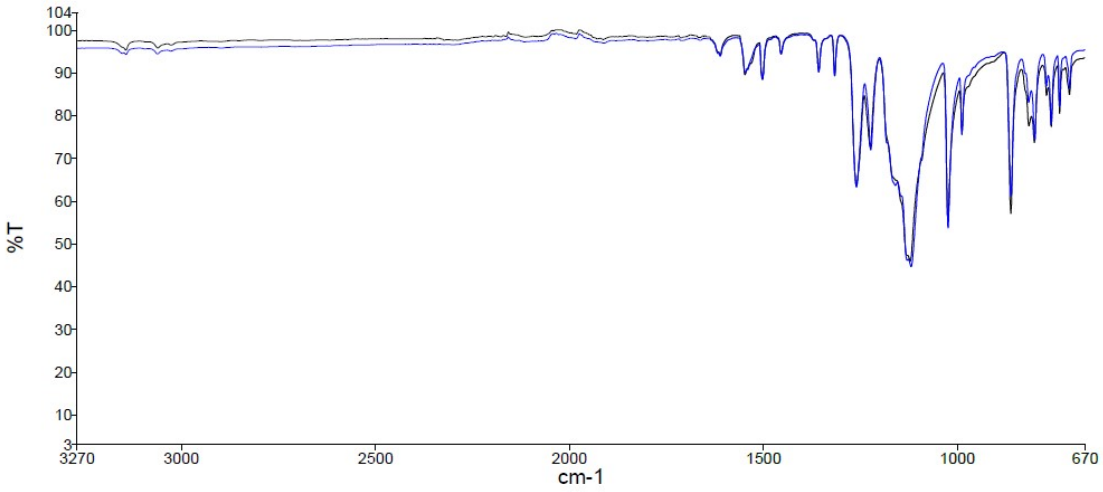
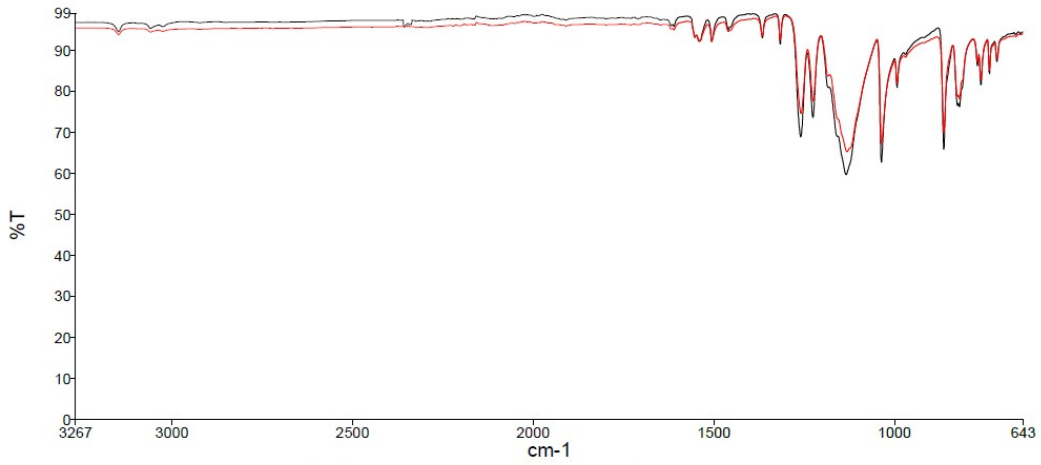


**Figure S4**. Superimposition of IR spectra recorded for the microcrystalline products **1** (a), **2** (b) and **3** (c) obtained by solvent-mediated syntheses and 10 minutes LAG (liquid-assisted grinding), recorded in the range 3200-700 $cm^{-1}$.

a)




b)




c)

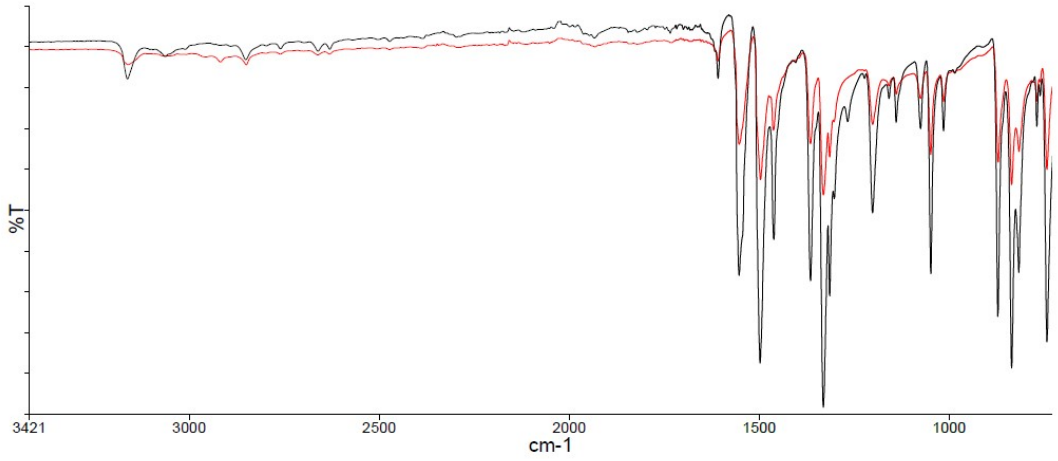
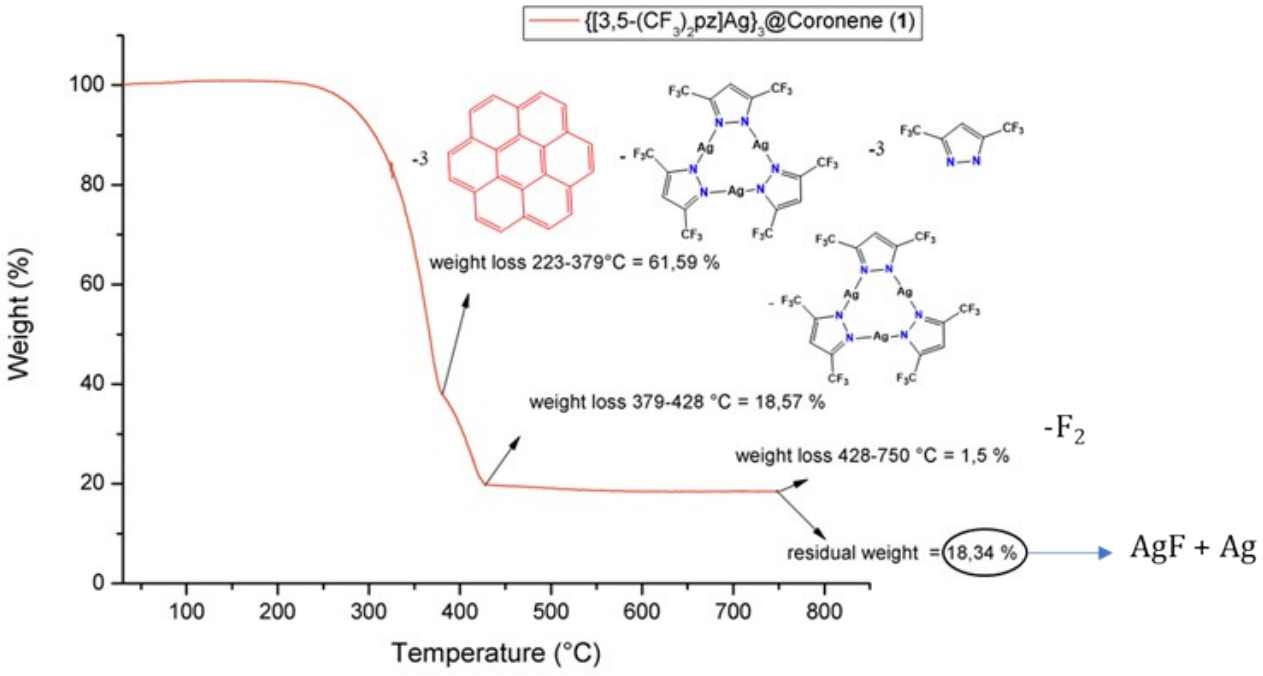


**Figure S5**. TGA plot with decomposition patterns of **1**,**2,** and **3** (from top to bottom).



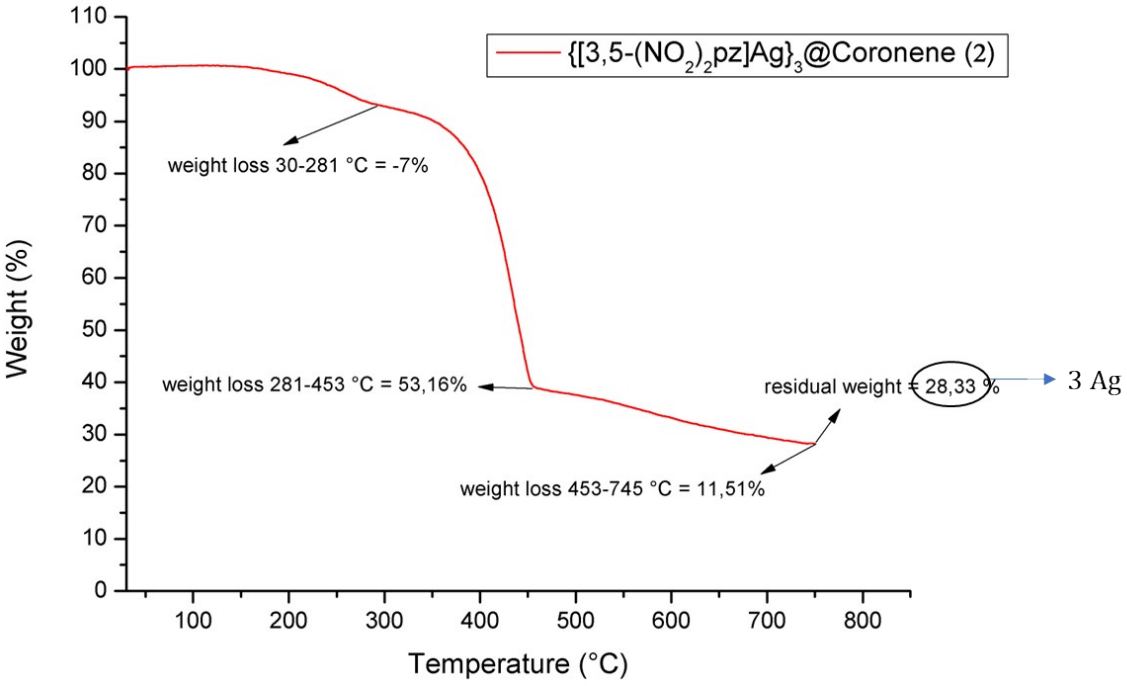




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**Figure 5S.** Continue.

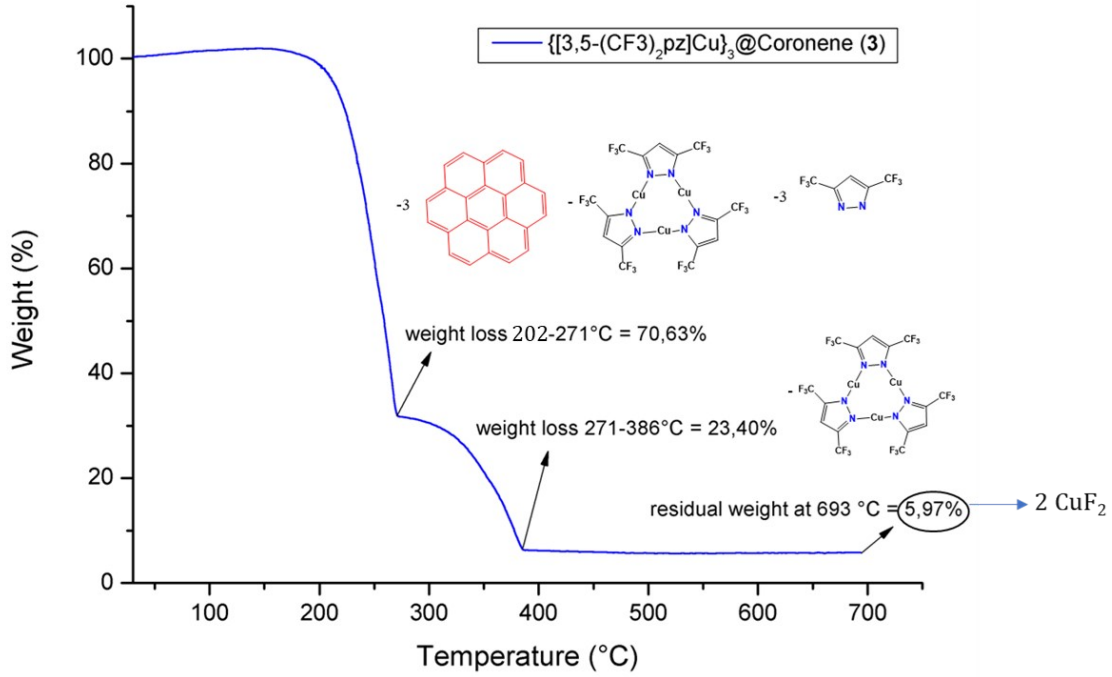
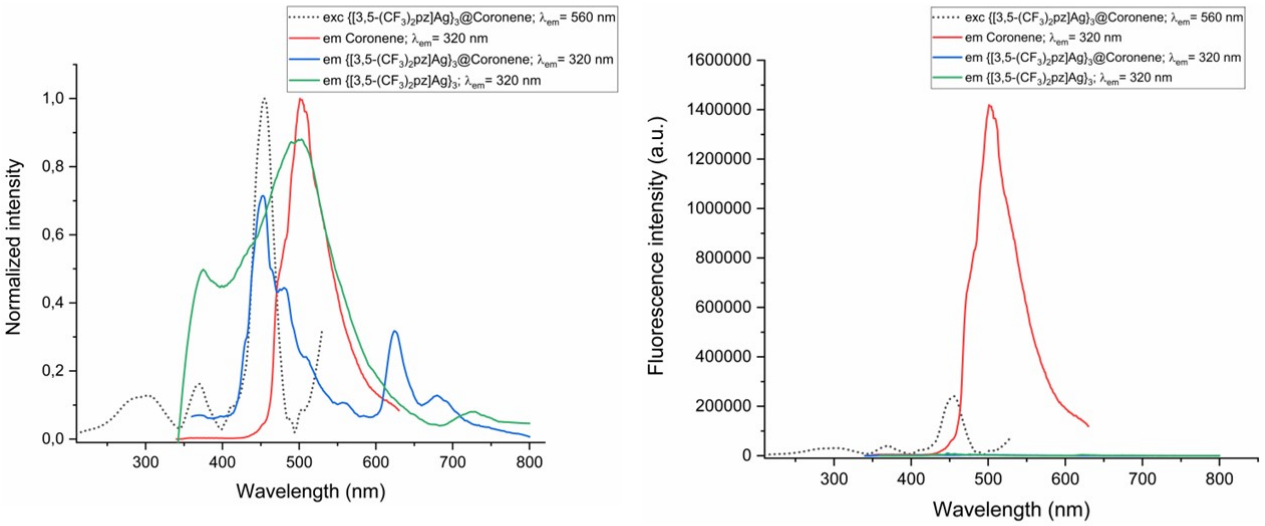


**Figure S6**. Normalized (left) and absolute (right) solid-state excitation/emission spectra of the adduct {[3,5-$(CF_3)_2$pz]Ag}$_3$@Coronene **1**, a), and {[3,5-$(NO_2)_2$pz]Ag}$_3$@Coronene, **2**, b) in comparison with the emission spectra of the starting compounds in the range 300-630 nm.

a)




b)

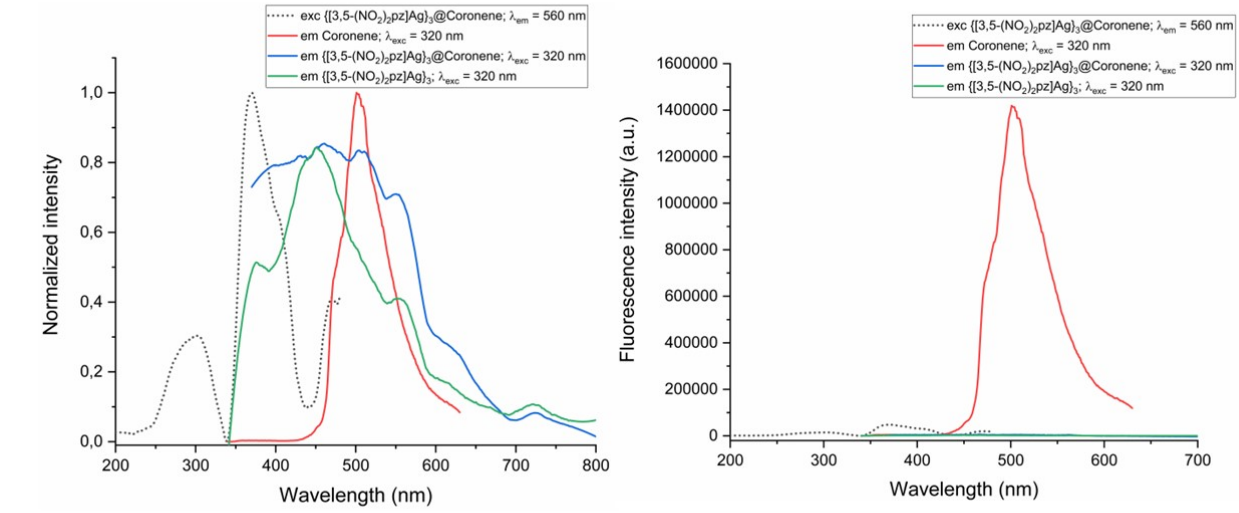


**Figure S7.** Solid state emission spectra of the coronene, of the $[(CF_3)_2pzCu]_3$ and of the adduct **3** upon excitation at 320 nm at room temperature.

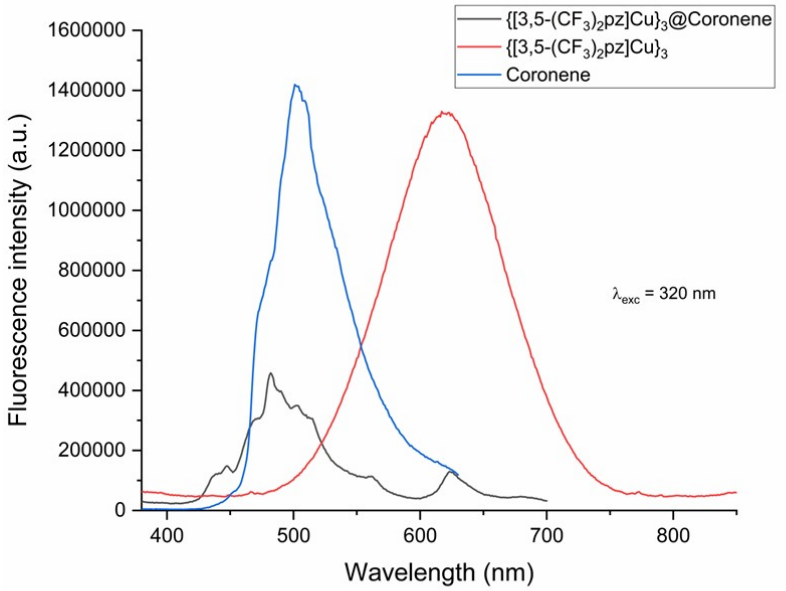


**Figure S8**. Normalized solid state excitation/emission spectra of the coronene/$[(CF_3)_2pzCu]_3$, adduct **3,** upon excitation at 320 nm, 360 nm and 400 nm. Upon excitation at 320 nm a weak emission at 560 nm is observed.

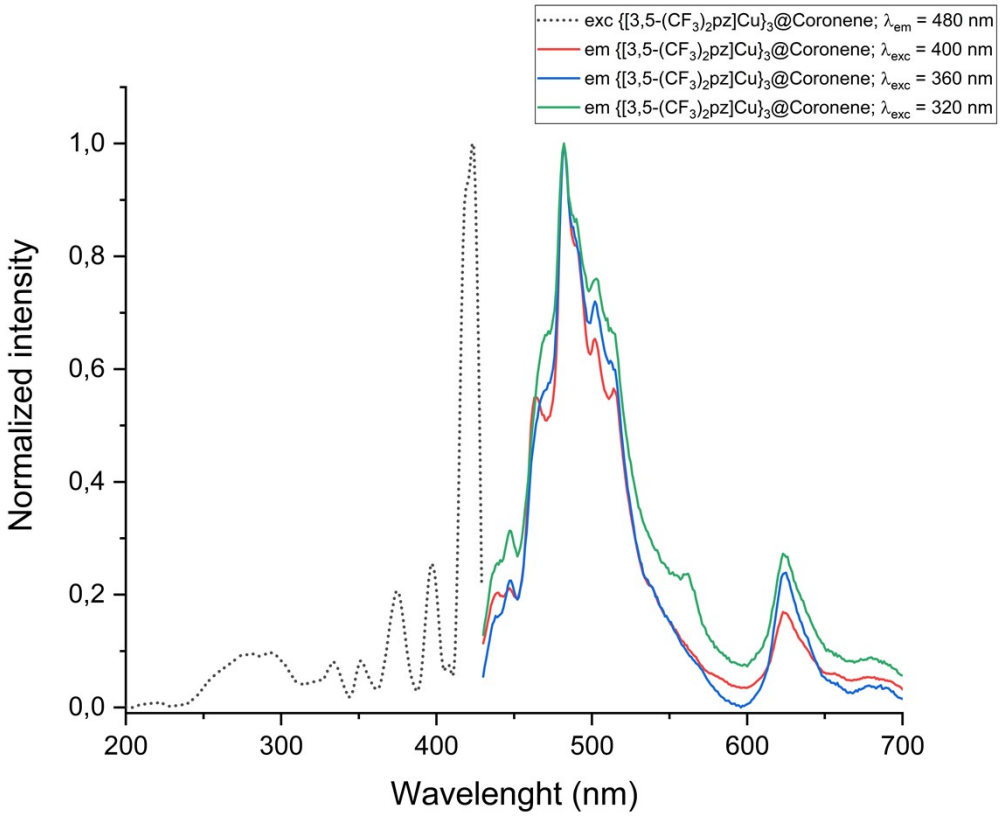
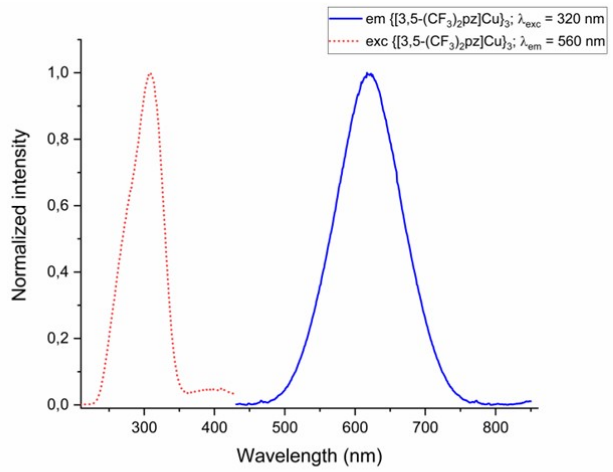
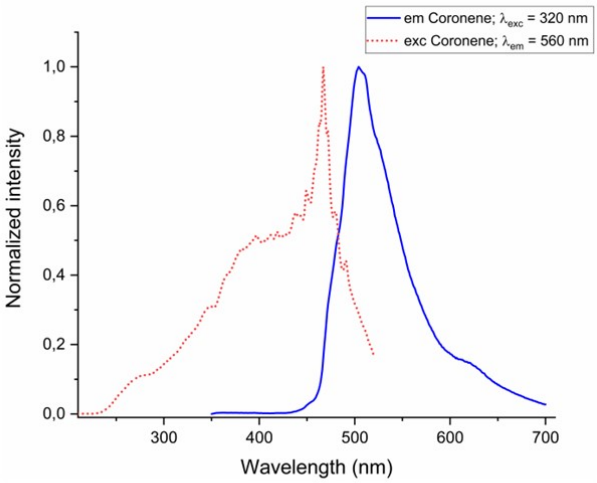
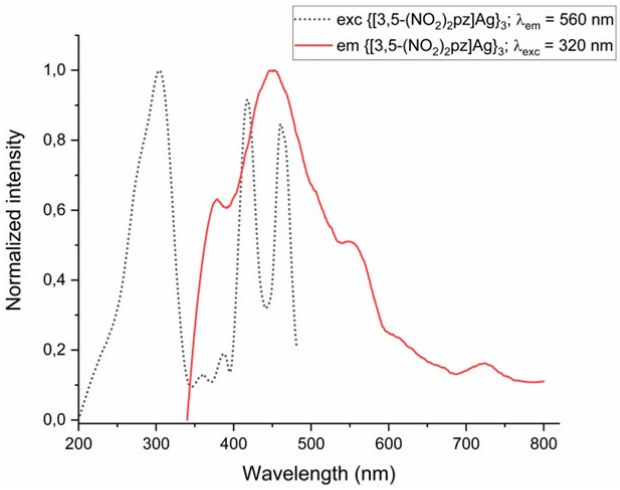


**Figure S9**. Excitation and emission spectra for $[(CF_3)_2pzCu]_3$, top left, for coronene, top right, for $[(NO_2)_2pzAg]_3$, bottom left, and for $[(CF_3)_2pzAg]_3$, bottom right.



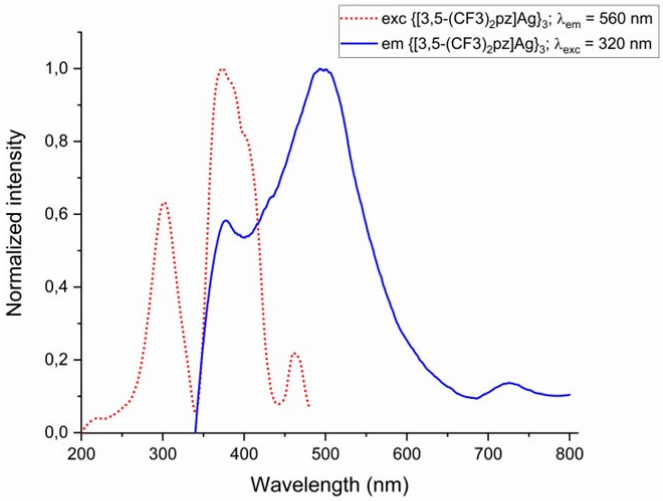



**Figure S10.** Emission bands obtained by exciting at 350 nm a 24.26 μM solution of coronene in DCM and upon titrating with a solution of $[(CF_3)_2pzCu]_3$ in DCM. The addition of the CTC was performed till a ratio of coronene: $[(CF_3)_2pzCu]_3$ almost 1:2 (first addition mole ratio $[(CF_3)_2pzCu]_3$/coronene = 0.269). The adding of $[(CF_3)_2pzCu]_3$ did not affected the intensity and emission maxima of coronene.

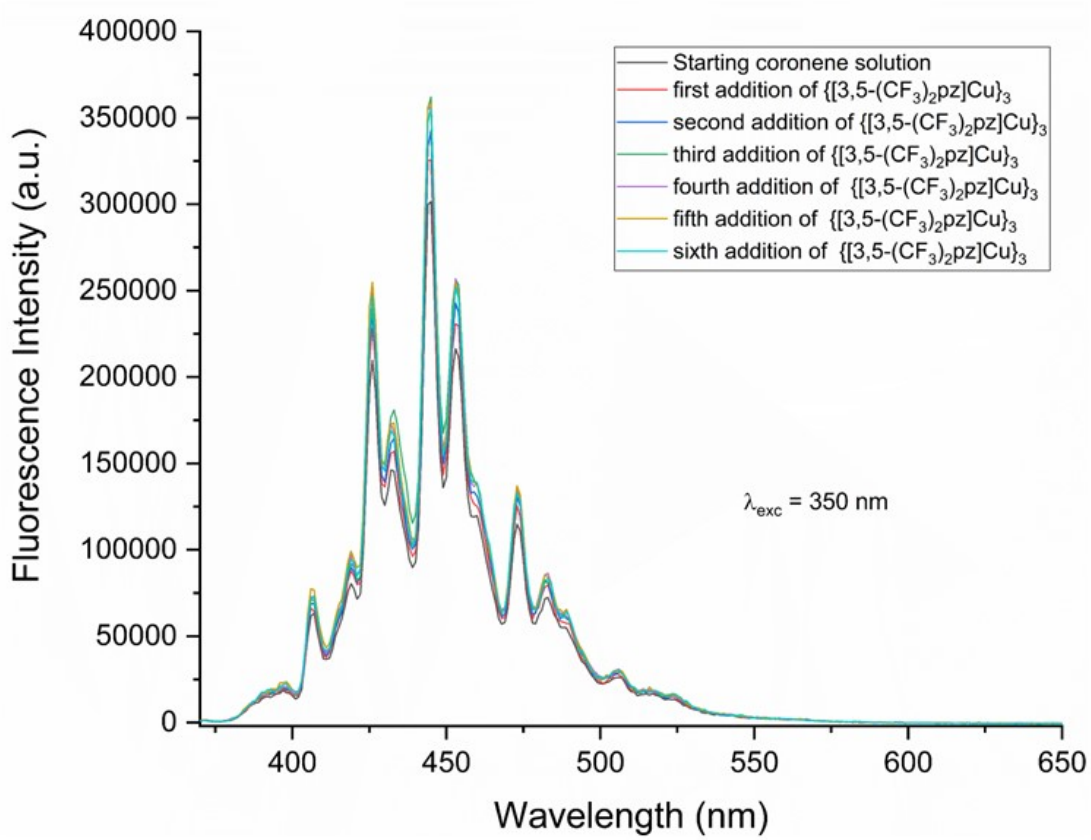



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**Figure S11**. Tauc plots of {[3,5-$(CF_3)_2$pz]Ag}$_3$ with direct (left) and indirect (right) band gap calculations.

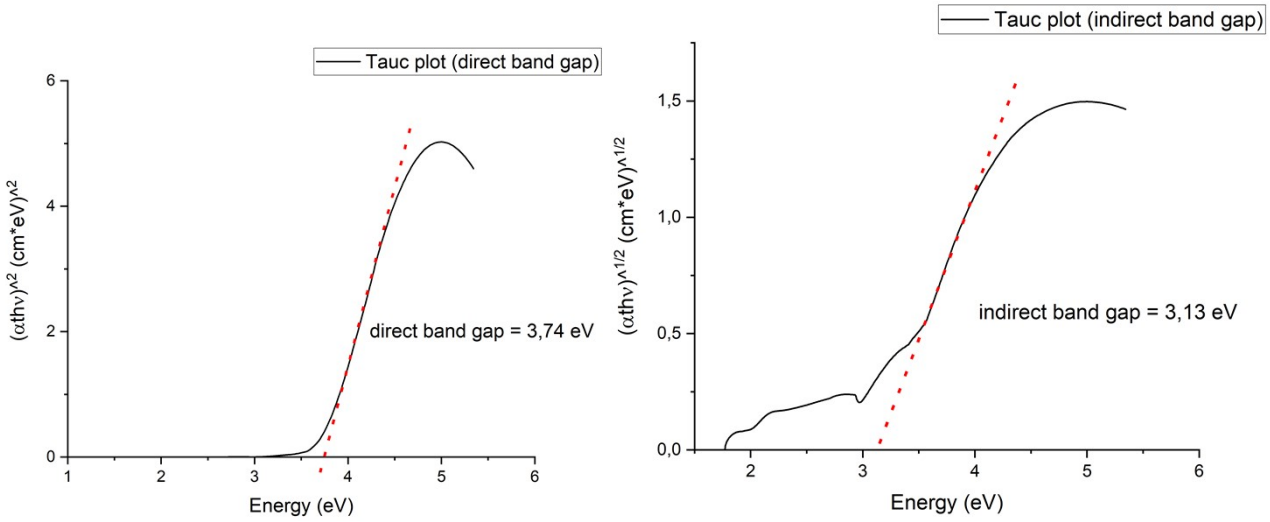
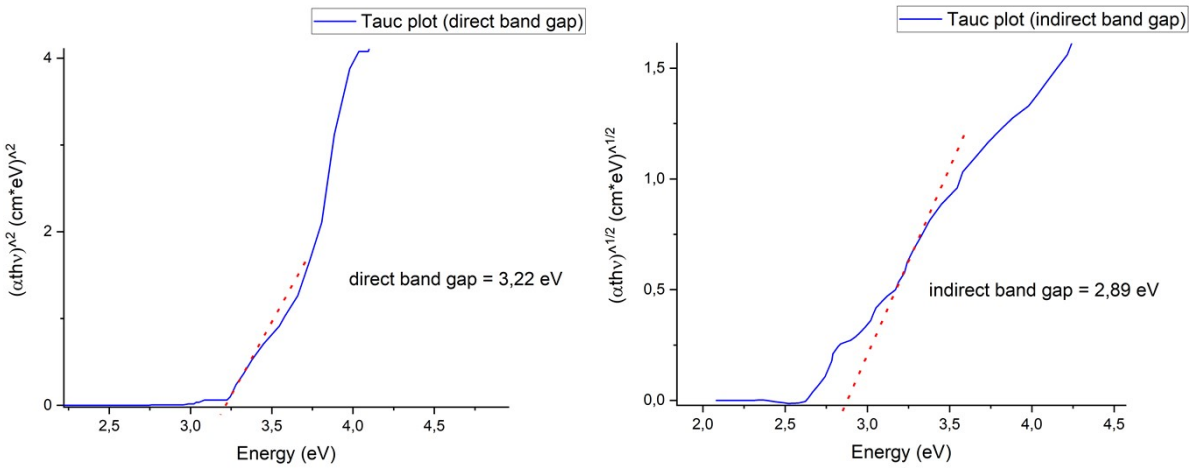



**Figure S12.** Tauc plot of coronene with direct (left) and indirect (right) band gap calculations.



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