# Surface doping of rubrene single crystals by molecular electron donors and acceptors

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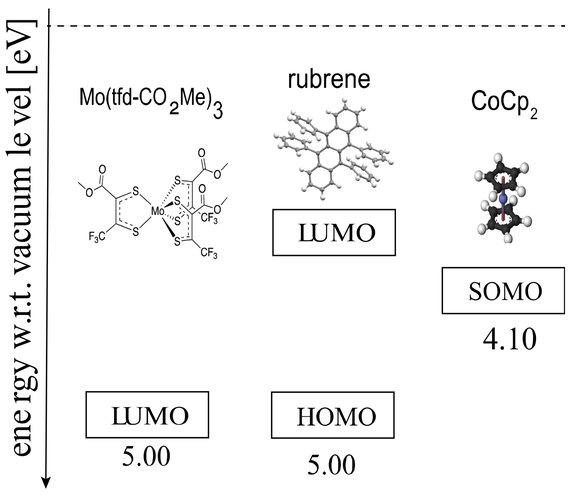
## Motivation

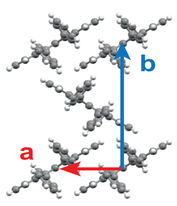
Organic electronic devices continuously require:
- efficient charge carrier injection
- higher charge carrier densities

Objectives are to investigate:
- surface molecular doping of organic single-crystals
- effect of surface doping on the electronic band structure

### Molecules and energy levels[1,2]




### Crystal structure[3]




| real space vector | | reciprocal space direction |
|---|---|---|
| a | ⟷ | Γ-Y |
| b | ⟷ | Γ-X |

### Fitting models[4]

- **Tight-binding model:**

$$E = E_c + 2t\cos(ak_{||}) \qquad m^*_{TB} = \frac{\hbar^2}{2ta^2}$$

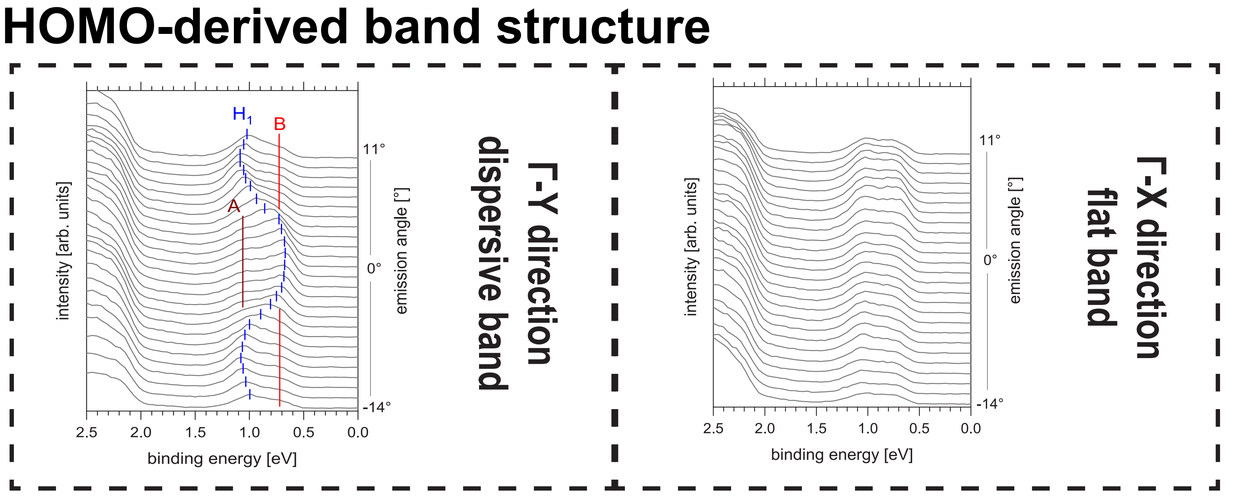
- **Nearly free electron model (parabolic):**

$$E = E_o + \frac{\hbar^2 k_{||}^2}{2m_p^*}$$

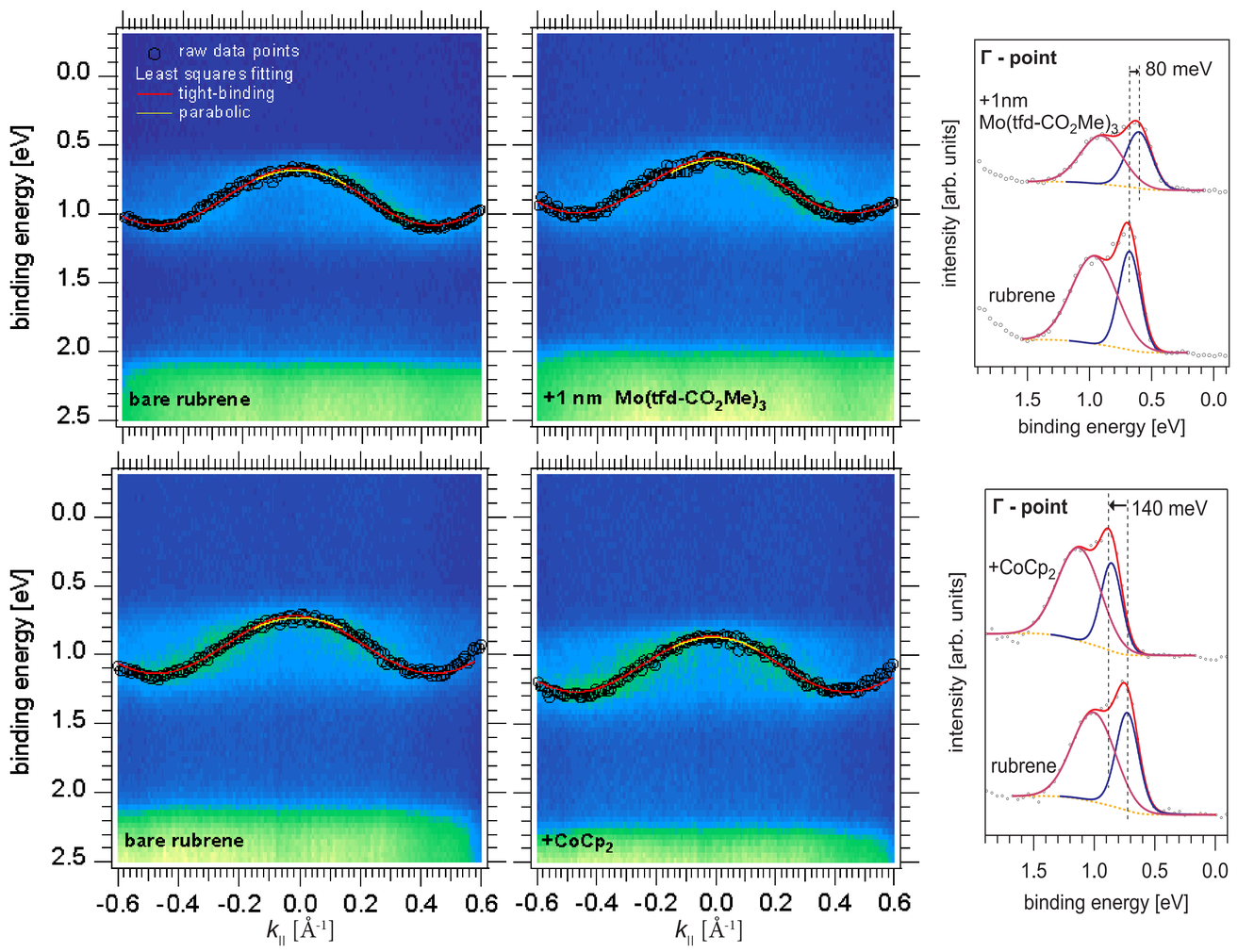
$E_c$: band center
$E_o$: band maximum
$t$: transfer integral
$a$: lattice constant
$m^*$: effective mass

## Experimental results

### HOMO-derived band structure




### Doping with electron donors and acceptors




| | *tight-binding* | | | | *parabolic* | | |
|---|---|---|---|---|---|---|---|
| | $E_C$ [eV] | $\Delta E_C$ [meV] | $t$ [meV] | $m^*_{TB}[m_0]$ | $E_0$ [eV] | $\Delta E_0$ [meV] | $m^*_p[m_0]$ |
| **bare rubrene** | 0.88 ± 0.05 | - | 103 ± 5 | 0.8 ± 0.1 | 0.69 ± 0.05 | - | 1.0 ± 0.2 |
| **+Mo(tfd-CO$_2$Me)$_3$** | 0.79 ± 0.05 | **90 ± 5** | 100 ± 5 | 0.8± 0.1 | 0.61 ± 0.05 | **80 ± 5** | 1.0 ± 0.2 |
| **bare rubrene** | 0.93 ± 0.05 | - | 105 ± 5 | 0.7 ± 0.1 | 0.73 ± 0.05 | - | 1.1 ± 0.2 |
| **+CoCp$_2$** | 1.07 ± 0.05 | **140 ± 5** | 101 ± 5 | 0.8 ± 0.1 | 0.87 ± 0.05 | **140 ± 5** | 1.0 ± 0.2 |

## Conclusions

- angle resolved time-of-flight photoemission experiments showed small but visible shifts in binding energy upon doping
- the small energy shifts can be explained by a Fermi level pinning scenario at the interface
- steric effects due to the bulkiness of the selected dopants could be a reason for the small shifts
- the HOMO-derived band and the band parameters remain essentially unperturbed

**References**: [1] Dai et al. Adv. Funct Mater., 2014, 24, 2197-2204 [3] Da Silva Filho et al. Adv. Mater., 2005, 17,1072-1076
[2] Chan et al. Chem. Phys. Lett., 2006, 431, 67-71 [4] Nakayama et al. J. Mater. Chem. C, 2020, 8, 9090-9132

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