Exciton Management in Supramolecular Polymers for Advanced Optoelectronic Applications.

M. A. Thottappali[1], Y. Panthi[1], A. Pandey[1], A. Chernyshev[2], J. Zedník[2], J. Vohlídal[2], J. Pfleger[1]

[1]*Institute of Macromolecular Chemistry CAS, Prague, Czech Republic.*

[2]*Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Prague, Czech Republic;*

Effective management of excitons relies on understanding the excited-state dynamics upon photoexcitation. This study explores the excited-state dynamics in a coordination polymer, $[CoU]_n$, formed through the self-assembly of 3,6-di(2,2′:6′,2″-terpyridin-4′-yl)-9-phenylcarbazole (U) with cobalt (II) (Co^{2+}) ions[1], in which the coordinated terpyridine (tpy) groups adopt a perpendicular arrangement around the Co^{2+} ions. The coordination alters the optical and electronic properties, like the energy band gap, and affects the exciton lifetime and dynamics [2]. Using femtosecond transient absorption spectroscopy, we analyzed metal - ligand charge transfer states and their impact on exciton dissociation and charge separation.

While comparing the time evolution of the excited-state spectra of the thin films, the $[CoU]_n$ complex exhibits an additional spectral feature compared to the broader transient response of Unimer (U). This suggests the formation of metal-to-ligand charge transfer (MLCT) states, leading to a modified exciton relaxation pathway. [3] The extended lifetime components in the complex imply a stabilized charge-separated state, likely influenced by ligand field effects and counterion interactions, which are crucial for electronic applications.

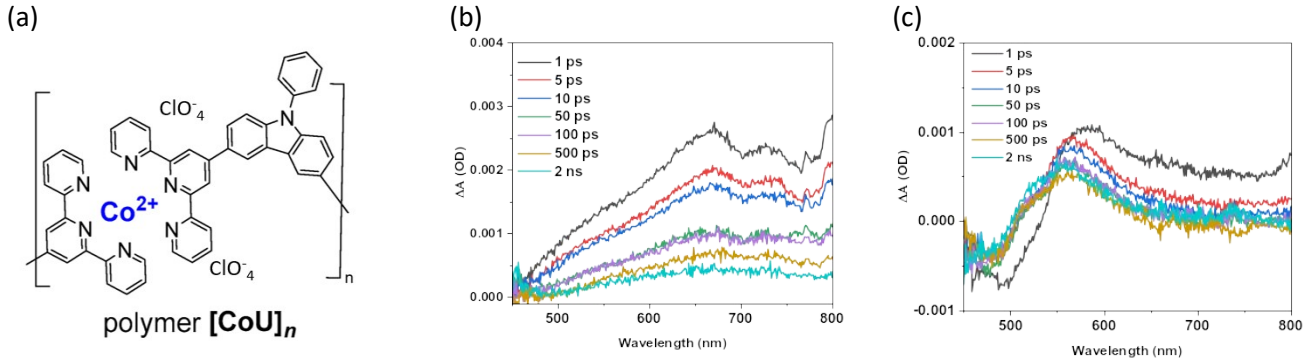

Fig. 1. (a) Scheme of metallo-supramolecular copolymer $[CoU]_n$, (b) Time evolution of transient absorption of thin film of U, (b) Time evolution of transient absorption of thin film of $[CoU]_n$ complex.

Acknowledgments

The work was financially supported by the MEYS of the Czech Republic, project LUAUS24032

References

[1] Pandey, A.; Chernyshev, A.; Panthi, Y.R.; Zedník, J.; Šturcová, A.; Konefał, M.; Kočková, O.; Foulger, S.H.; Vohlídal, J.; Pfleger, J. Synapse-Mimicking Memristors Based on 3,6-Di(tpy)-9-Phenylcarbazole Unimer and Its Copolymer with Cobalt(II) Ions. Polymers 2024, 16, 542.

[2] Owen, M.E.; Carter, E.; Hutchings, G.J.; Ward, B.D.; Murphy, D.M. Influence of Counterions on the Structure of Bis(Oxazoline)Copper(Ii) Complexes; an EPR and ENDOR Investigation. Dalt. Trans. 2012, 41, 11085–11092.

[3] Roy, S.; Roy, S.; Saha, S.; Majumdar, R.; Dighe, R.R.; Jemmis, E.D.; Chakravarty, A.R. Cobalt(II) Complexes of Terpyridine Bases as Photochemotherapeutic Agents Showing Cellular Uptake and Photocytotoxicity in Visible Light. Dalt. Trans. 2011, 40, 1233–1242.