

## Polymer and Colloid Highlights

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### Polymers with Exceptional Photoluminescence by Homoconjugation

Andreas Braendle, Aleksandr Perevedentsev, Nathan J. Cheetham, Paul N. Stavrinou, Jörg A. Schachner, Nadia C. Mösch-Zanetti, Markus Niederberger, and Walter Caseri\*

\*Correspondence: Prof. W. Caseri, Department of Materials, ETH Zürich, E-mail: walter.caseri@mat.ethz.ch

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Commonly, photoluminescence in organic polymers relies on  $\pi$ -electron delocalization by alternating double and single bonds. Remarkably, however, poly(phenylene methylene) (PPM) and methyl-substituted derivatives, such as those shown in Fig. 1a, exhibit fluorescence in the wavelength region of 400–600 nm which cannot be explained by such systems of delocalized electrons.<sup>[1]</sup> Instead, the results of extended investigations are in line with homoconjugation as the origin of the photoluminescence between 400 nm and 600 nm.<sup>[1]</sup>

Homoconjugation only arises in special chemical structures for which conjugation across individual  $\pi$ -electron systems can

occur despite those systems being separated by an electronically insulating group, e.g. a methylene group.<sup>[2–4]</sup> Such a conjugation is enabled by the overlap of p-orbitals in PPM (and derivatives), as schematically illustrated in Fig. 1b. DFT calculations for PPM indicate that homoconjugation is indeed energetically favorable.<sup>[1]</sup> Note that homoconjugation in PPM and its derivatives can only be effective in certain conformations of the polymer chains, such as that displayed in Fig. 1b. For example, it appears that the conformations in the as-synthesized materials, which were finally obtained by rapid precipitation, are frozen in non-optimal geometries for homoconjugation because absorption and fluorescence intensity for such samples markedly increase following annealing above the glass transition temperature (66 °C for PPM; onset of thermal decomposition by TGA at 470 °C).

Fluorescence of PPM and its derivatives is observed in the solid (Fig. 1c) as well as in the dissolved states. The polymers were extensively studied by UV-vis absorption spectroscopy, photoluminescence excitation spectroscopy and cyclovoltammetry. The HOMO-LUMO gap of 3.2–3.3 eV corresponds to an onset of optical absorption at approximately 375–390 nm, i.e. at higher wavelengths than expected for isolated phenylene groups. This is in agreement with homoconjugation for which electron delocalization occurs over several phenylene units. Further to this, the observed peak shifts of photoluminescence spectra towards higher wavelengths with increasing degree of polymerization (DP), up to DP  $\approx$  10, are fully consistent with electron delocalization along the polymer backbone. The photoluminescence lifetime recorded for thin PPM films is remarkably high, namely 8.55 ns. The photoluminescence quantum efficiency in solutions amounts to 69% and in films to 41%; notably the latter value is comparable to those for high-performance  $\pi$ -conjugated polymers. Interestingly, however, the absorption coefficient of PPM, measured for thick films, amounted to 80 cm<sup>-1</sup> which, for comparison, is about 2600 times lower than the value of poly(dioctylfluorene).<sup>[5]</sup>

Notably,  $\pi$ -stacking, aggregation/crystallization and impurities were excluded as the origins of fluorescence in the course of the extended investigations.<sup>[1]</sup>

We expect that poly(phenylene methylene) and its derivatives will serve as examples of a new class of fluorescent polymers characterized by homoconjugation along the main chain.

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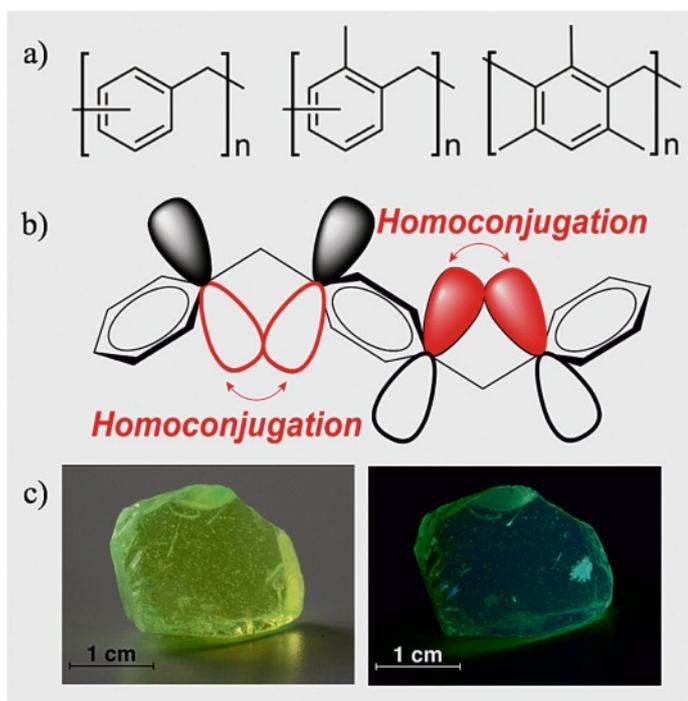


Fig. 1 a) Structures of PPM and two of its derivatives, b) schematic illustration of homoconjugation in PPM, c) images of a photoluminescent PPM sample under ambient light (left) and UV-light (right).

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If you are interested in submitting a new highlight, please contact:

Prof. Dr. Markus Niederberger, Department of Materials, ETH Zürich  
E-mail: markus.niederberger@mat.ethz.ch, Tel.: +41 44 633 63 90