4. Long-Wavelength Fluorescence Properties of Thiol-containing Imide Compound via Excited-State Intramolecular Proton Transfer

Riku OTA, Yuka ANDO, Rika WATANABE, Haonan LIU, Shinji ANDO*

Department of Chemical Science and Engineering, Institute of Science Tokyo, Japan
*ando.s.aa@m.titech.ac.jp

Abstract: Highly fluorescent imide compounds and polyimides[1–4] are expected to be applied as solar wavelength conversion films due to their controllable optical properties with multi-color emissions, excellent heat resistance, and mechanical strength. For practical applications, further enhancement of Stokes shift (SS), which is the difference between the excitation and fluorescence wavelengths, and an increase in quantum yield are demanded. Excited-state intramolecular proton transfer (ESIPT) is a phenomenon in which proton transfer occurs within the molecule upon exposure to excitation light, causing the molecular structure to undergo tautomerization from the normal form (N*) to the tautomeric form (T*), resulting in long-wavelength fluorescence. This mechanism is effective for expanding SS (Fig. 1). In our research group, we have developed a series of imide compounds incorporating phenolic hydroxyl (–OH) [2] or alkylamino (–NHR) [3] groups and reported their long-SS fluorescence properties via the ESIPT process. Furthermore, naphthalene diimide compounds containing thiol groups (–SH) were newly developed [4], exhibiting red fluorescence via ESIPT and showed significant changes in emission wavelength in response to the environment, compared to conventional ESIPT compounds. In this study, aiming to further expand the SS to the deep-red and near-IR regions, an imide compound containing two thiol groups (2SPM-IC, Fig. 2) was newly designed and synthesized. We are focusing on the intriguing fluorescence properties possibly resulting from the double proton transfer (ESDPT) phenomenon and investigated its fluorescence properties in the solid state and solution.

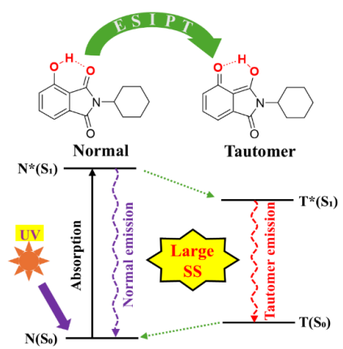

Fig. 1 Mechanism of long Stokes-shifted fluorescence via ESIPT.

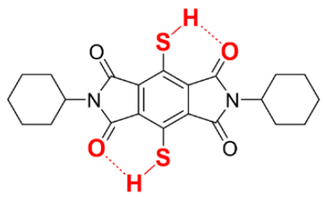

Fig. 2 Structure of 2SPM-IC.

Keywords: **Polyimide, ESIPT, Thiol group, ESDPT**

[1] J. Wakita, H. Sekino, K. Sakai, Y. Urano, S. Ando, J. Phys. Chem. B, 19, 15212 (2009).
[2] J. Wakita, S. Inoue, N. Kawanishi, S. Ando, Macromolecules, 43, 3594 (2010).
[3] A. Tabuchi, T. Hayakawa, S. Kuwata, R. Ishige, S. Ando, Mater. Adv., 2, 5629 (2021).
[4] Y. Ando, M. Doi, H. Liu, S. Ando, J. Mater. Chem. C, DOI:10.1039/D5TC01389E (2025).

5. Synthesis of a novel ABA triblock copolymer with semiaromatic polyimide and polyisobutene segments

Toshinobu Sato, Tomoya Higashihara*

Graduate School of Organic Materials Science, Yamagata University,
Yonezawa, Yamagata, Japan.
thigashihara@yz.yamagata-u.ac.jp

Abstract: Recently, the demand for interlayer dielectric films for high-frequency applications, such as 5G/6G communication devices, has increased. However, conventional wholly aromatic polyimides (PI)s, typical super-engineering plastics with excellent mechanical properties, high heat, and chemical resistance, do not meet the required dielectric constant (D_k < 3) for applying to insulating materials in such devices, necessitating the development of low-D_k PIs. From an environmental point of view, the development of non-fluorinated low-Dk PIs (D_k < 3) has become a challenging topic. Notably, the dielectric tangent (D_f) values should decrease simultaneously while developing low-Dk materials.
In this study, we developed a synthetic method for a novel non-fluorinated ABA-type triblock copolymer, PIB-b-PI-b-PIB, where A and B were polyisobutene (PIB) prepared by living cationic polymerization of isobutene and PI prepared by the statistical ternary copolymerization using 4,4- oxydianiline (ODA), bis(4-aminocyclohexyl)methane (PACM), and 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA) (ODA:PACM:CBDA = 0.25: 0.75: 1, by mol.), respectively. The obtained copolymer exhibits excellent dielectric properties, a high Dk of 2.82 and a low Df of 0.0111 at 10 GHz, while maintaining high thermal stability (5% weight loss temperature, $Td_{5\%}$ > 380 °C). It was found that the introduction of PIB effectively reduced in-plane dipole orientation polarization and electronic polarization, as calculated from the refractive index and D_k values of PIB-b-PI-b-PIB. This could be attributed to a decrease in the composition of the imide group, which consists of polar groups, by incorporating PIB segments, ultimately leading to low D_k values. These findings suggest that incorporating PIB segments into PI is a promising molecular design strategy for reducing D_k while maintaining low D_f and thermal stability.

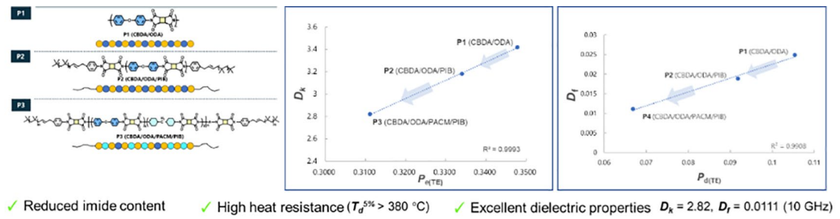

Figure 1. Chemical structures and dielectric properties of P1–P3.

Keywords: **polyimide, polyisobutene, low-dielectric, dielectric tangent, block copolymer**
Acknowledgements: We thank Prof. Shinji Ando at Institute of Science, Tokyo, for supporting the dielectric measurements.

[1] Higashihara, T. et al. Japan Patent, 2022, 2022-169849.
[2] Ojiha, U. et al. Macromolecules, 2008, 41:3832–3841.