

COMMUNICATION

A Spin-Active, Electrochromic, Solvent-Free Molecular Liquid Based on Double-Decker Lutetium Phthalocyanine Bearing Long Branched Alkyl Chains

Agnieszka Zielinska,^[a,b] Atsuro Takai,^[a] Hiroya Sakurai,^[a] Akinori Saeki,^[c] Marcin Leonowicz,^[b] and Takashi Nakanishi^{*[a]}

Abstract: Synthesis and characterization of a novel, multifunctional, solvent-free room-temperature liquid based on alkylated doubledecker lutetium (III) phthalocyanine (Pc₂Lu) are described. Lowering of the melting point and viscosity of intrinsically solid Pc2Lu compounds has been achieved through the attachment of flexible, bulky, and long branched-alkyl chains, i.e. 2-octyldodecyl, to the periphery of the Pc₂Lu unit. The embedded Pc₂Lu unit maintains its inherent molecular functions, such as spin-active nature and electrochromic behavior in the liquid state. Comparison of the properties with a solid-like Pc2Lu derivative, functionalized with shorter alkyl chains, i.e. 2-ethylhexyl, underlines the importance of the hampering effect on the $\pi-\pi$ interactions of neighboring Pc₂Lu molecules by bulkier and longer branched-alkyl chains. This study could possibly pave the way for novel multifunctional liquids whose spin-activities are associated with their rheological or optoelectronic properties.

Solvent-free functional molecular liquids (FMLs) are a novel category of organic soft materials.^[1,2] FMLs are created by combining the advantages of fluids (e.g. excellent processability, independent surface geometry, capillary action into confined space, deformability, and amorphousness) with various functions based on the core molecular component. In particular, FMLs comprising optoelectronically-active π -conjugated molecular units exhibit luminescence,[3-5] photoconductivity,[5-8] and nonlinear optics.^[9] The design strategy behind those FMLs is simple in principle: the functional core unit, such as a π -conjugated molecule, including even large macrocycles such as porphyrin (Por)^[10,11] and phthalocyanine (Pc),^[9,12] is embedded by peripherally bulky and flexible alkyl or silyl side-chain substituents. As a result, the intrinsically solid and rigid π -conjugated molecules can be turned into a liquid at room temperature. More importantly, this strategy can lead to isolation of the functional core unit by steric repulsion of the alkyl chains; therefore, prediction of the bulk optoelectronic properties as neat material can be simply

 [a] A. Zielinska, Dr. A. Takai, Dr. H. Sakurai, Dr. T. Nakanishi Frontier Molecules Group, International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS)
 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan E-mail: NAKANISHI.Takashi@nims.go.jp
 [b] A. Zielinska, Dr. M. Leonowicz Warsaw University of Technology ul. Wołoska 141, Warsaw 02-507, Poland

 [c] Dr. A. Saeki Department of Applied Chemistry, Graduate School of Engineering, Osaka University

2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

Supporting information for this article is given via a link at the end of the document.

transferred from the inherent molecular functions of the $\pi\text{-}$ conjugated core.

Numerous studies of alkylated π -molecules have proven that the substitution pattern, length, and level of branching of alkyl chains are very important factors for determining the bulk properties.^[13,14] The bulky alkyl chains can protect the functional core moiety from photodegradation.^[3b] Further adjustment of the optoelectronic properties of alkylated π -FMLs by doping of π conjugated molecular additives has also been achieved.[3-5,7,15,16] The lack of necessity of polymer matrix or solvent can allow higher concentration/density of functional π -units in the neat liquid, and may also help with the fabrication of thin films or highly defined elements in confined spaces. Therefore, we believe the core isolated and protected alkylated *π*-FMLs can lead to the creation of various new soft materials with predictable optoelectronic functions. The functions we focus on in this study are spin behavior, magnetic property, and electrochromism of a neutral radical at the highly dense solvent-free liquid states.

A double-decker lutetium (III) phthalocyanine (hereafter abbreviated as Pc_2Lu) was chosen as the functional core unit because of its spin-active nature, electrochromic properties,^[17,18] and paramagnetic behavior.^[19–21] Pc_2Lu is a neutral radical composed of one Lu^{3+} and two Pc^{2-} macrocycles, with a hole delocalized over the Pc rings. Unsubstituted Pc_2Lu is a crystalline solid material with limited solubility in most common organic solvents, which makes its synthesis, processing, and application more problematic. Pc_2Lu derivatives substituted with linear alkyl chains have a strong tendency to self-assemble into columnar liquid crystalline structures, favorable for semiconducting applications.^[22] However, soft condensed matter with Pc_2Lu units possessing intrinsic spin-radical characteristics at room temperature has never been achieved. Here, we develop an FML based on the spin-radical functions of alkylated Pc_2Lu .

Solvent-free, room-temperature liquid Pc₂Lu was synthesized by substituting the Pc macrocycle with bulky and flexible branched long alkyl chains, i.e. thio-2-octyldodecyl chains, at the β -position (1a. Figure 1a). As a reference solid compound, Pc₂Lu bearing shorter thio-2-ethylhexyl chains was also synthesized (1b. Figure 1a). In both cases, racemic isomers of Guerbet alcohol^[23,24] based branched alkyl chains were chosen, due to their potential for lowering the melting point and/or decreasing the viscosity of liquid substances.^[25] The target **1a** is a brown viscous fluid, while the reference 1b is an amorphous solid at room temperature (see Scheme S1 for synthetic details). Both 1a and 1b were characterized by ¹H NMR (Figure S1), UV-vis absorption spectroscopy (vide infra), and matrix-assisted laser desorption/ionization time-of-flight mass (MALDI/TOF-MS) analysis (Figure S2).

Differential scanning calorimetry (DSC) was applied to evaluate the thermal behavior of **1a** and **1b** (Figure 1b and Figure S3). In the case of **1a**, only one clear transition, from a glassy

COMMUNICATION



Figure 1. a) Chemical structures of 1a (R = 2-octyldodecyl) and 1b (R = 2-ethylhexyl). b) The heating trace of DSC thermograms of 1a: first heating (solid line), 1b: first heating (dotted line), and second heating (dashed line).

state to an isotropic state, was observed below 223 K. On the other hand, 1b exhibited solid to isotropic liquid transition with a melting point (T_m) at 332 K ($\Delta H = 27.99 \text{ kJ mol}^{-1}$, $\Delta S = 0.48 \text{ kJ}$ mol⁻¹ K⁻¹) in the first heating trace. This transition disappeared in the second heating trace, and instead a glassy transition appeared below 253 K. This behavior is typical for the supercooling phenomenon, where the kinetically trapped supercooled liquid state does not quickly organize into a solid state.^[26] The thermodynamically stable solid state of 1b can be obtained after thirteen additional days of storage at 278 K, which would be the origin of the solid showing melting transition on the first heating process. This process has been visualized by polarized optical microscopy (POM), as shown in Figure S4. These results indicate that the branched chains significantly lower the transition temperatures to form a new type of fluid matter of Pc₂Lu compounds - rather thermodynamically stable roomtemperature liquid or kinetically trapped supercooled liquid, which is totally different from the other linear alkyl- or alkyloxysubstituted lanthanide Pc.^[27-32]

To acquire further insight into the unique phase behavior of branched alkylated Pc_2Lu , small- and wide-angle X-ray scattering (SWAXS) measurements were conducted. In the SWAXS profile of **1a** measured at 298 K, two broad halos were observed (Figure S5). The halo in the small-angle region, appearing around the *q* value of 2.7 nm⁻¹ (~23 Å in length), corresponds to the average

core–core distance between the Pc₂Lu units that are separated by disordered bulky alkyl chains. The halo signal is a much broader feature compared with that of liquid crystalline examples,^[22,27,28] indicating inhomogeneity in the core–core distance and conformations. The molten alkyl chains can be observed as a broad halo in the wide-angle region (maximum at around 13 nm⁻¹ of *q*, ~4.8 Å in length). This SWAXS result well reflects the disordered state and absence of long-range ordered structure in **1a**. In contrast, the SWAXS profile of the semi-solid sample of **1b** at 298 K shows several sharp peaks overlaid on two broad halos, representing the coexistence of amorphous and crystalline states (Figure S6 and Table S1).^[27,28] It should be noted that the halo in the small-angle region at 3 nm⁻¹ of *q* (~20 Å in length) corresponds to the core–core distance between the Pc₂Lu units, which is a shorter space than that seen in **1a**.

The fluid character of 1a has been evaluated by means of the rheology technique. The dependence of the storage modulus (G') and loss modulus (G') as a function of the strain amplitude (γ) at 296 K is presented in Figure 2a. In the strain range below 0.5%. G' and G" showed similar values, while above 0.5%, G" exceeded G', which indicates the liquid nature of 1a. This liquid characteristic with a shear-thinning feature has been further confirmed by measuring the complex viscosity (η^*) varying under different γ at 296 K (Figure 2b). This behavior was also present in the temperature dependent study. The moduli (G', G'') were obtained as a function of the angular frequency (a) at 296 K, and in the temperature range of 298–328 K for $\gamma = 25\%$ (Figures S7– S10). All the results confirm that 1a has non-Newtonian liquid characteristics with a shear-thinning feature. A similar non-Newtonian liquid phenomenon was seen in linear alkyl chain substituted liquid Por^[10,11] and Pc.^[12] Both alkylated Por and Pc liquids contain relatively large *π*-conjugated macrocycles that might maintain subtle π - π interactions in their liquid state.

Both in the neat state and in solution, 1a and 1b exhibit a deep brown color in their neutral state (Figure S11). The brown color of the neutral Pc₂Lu molecules, as opposed to the usually reported green for the neutral Pc2Lu, is the result of the thioalkyl chains' influence on the molecular energy levels.[18] UV-vis absorption spectroscopy for 1a and 1b was performed in chloroform, dichloromethane, tetrahydrofuran (THF), and n-hexane. In the case of the THF solution of 1a and 1b, the color gradually changed from brown to blue. The absorption spectral change (Figure S12) corresponds to the reduction of the neutral Pc₂Lu complex. One possible explanation could be the high donor number of THF (84 kJ mol-1);[33] similar behavior has been reported for Pc2Tb in THF.[34] Absorption bands of the neat samples of 1a and 1b measured with a solid powder matrix of BaSO₄ do not differ significantly, but are broader than those in solution (Figure S11). These results indicate nonspecific, random interactions between the core Pc₂Lu in the solvent-free state, which is consistent with the results of SWAXS and rheology. In addition, these limited $\pi - \pi$ interactions among neighboring Pc₂Lu units were confirmed by POM observation, in the form of nonlong-range ordering in 1a and 1b.

Although largely overlapped π -systems seen in liquid crystalline alkylated Pc₂Lu compounds are known as good n-type semiconductors,^[22] the less ordered liquid **1a** and semi-solid **1b**

10.1002/asia.201800175

WILEY-VCH

COMMUNICATION



Figure 2. a) Rheology results of **1a** at 296 K. Storage (*G*', red circles) and loss (*G*" blue squares) moduli vs. strain amplitude (γ). Inset of a) is a photo image of **1a** at 296 K under visible daylight. b) Complex viscosity (η^*) vs. angular frequency (ω) of **1a** at 296 K for different values of strain amplitude (γ).

exhibited relatively low photoconductivity, which was evaluated by means of flash photolysis time-resolved microwave conductivity (FP-TRMC) at 298 K, as shown in Figure S13.^[35,36] The photoconductivity maximum ($\phi\Sigma\mu_{max}$) of the liquid **1a** was only 1.9×10^{-6} cm² V⁻¹ s⁻¹, about one-third the $\phi\Sigma\mu_{max}$ value of the solid **1b** ($\phi\Sigma\mu_{max} = 5.1 \times 10^{-6}$ cm² V⁻¹ s⁻¹). These results also indicate that the core–core interactions of **1a** are substantially, but not completely, hampered by attached bulky and branched long alkyl chains, which is consistent with their structural analyses.

Electron spin resonance (ESR) and superconducting quantum interference device (SQUID) measurements were carried out for the spin characteristics of 1a and 1b. ESR spectra in dichloromethane (10⁻⁴ M) solution and the spectrum of the liquid 1a at room temperature exhibited an ESR signal at g = 2.0027 ± 0.0002 and wide peak widths of about 0.9 \pm 0.1 mT, while the semi-solid 1b had a much narrower peak width of 0.1 mT at $g = 2.0028 \pm 0.0002$ (Figure 3a). The observed difference in the peak width between 1a and 1b in their solvent-free samples can be understood as an effect of the Pc₂Lu's core conditions. The bulkier and longer branched alkyl chains on 1a contribute to sufficient weakening of the Pc2Lu-Pc2Lu interactions. On the other hand, the shorter alkyl chains on 1b do not provide an effective barrier between adjacent Pc2Lu units. Therefore, interactions between the neighboring spin-active species are not limited, which leads to narrowing of the ESR signal.^[18a,37,38] The magnetic

susceptibility as a function of the temperature was measured in both 1a and 1b in their solvent-free state. The plots have been fitted to match the Curie-Weiss law between 10 and 400 K for both samples, indicating their paramagnetic behavior (Figure S14). This result is consistent with the variable-temperature ESR measurements in the range of 4.2-400 K (Figures S15 and S16). The values of Curie constant C, 0.297 emu K mol⁻¹ for 1a and 0.262 emu K mol⁻¹ for 1b, are similar to the ones reported for other Pc₂Lu complexes.^[39] The Weiss temperature, Ø, was estimated to be $\Theta = -0.12$ K for **1a** and -0.87 K for **1b**. These values are very close to zero, suggesting almost no magnetic interaction in these compounds. It may be noticed that these values are approximately 200 times smaller than the typical values of $\Theta \sim 30$ K observed for other Pc₂Lu compounds.^[39-41] This difference may be caused by the difference in the core-core distance between Pc₂Lu units. Thus, the Weiss temperatures also support that our Pc₂Lu molecules, in particular 1a, are randomly dispersed even in the neat state.

The electrochromic feature is an attractive property of Pc₂Lu based materials. Cyclic voltammograms (CVs) of both 1a and 1b in dichloromethane solution are shown in Figure S17. Both 1a and 1b showed five redox states: neutral, three reduced states, and one oxidized state. The redox potential values are almost independent of the side chain length (Table S2). Spectroelectrochemistry results are presented in Figures 3b, 3c, S18, and S19. Note that each process was reversible. During reduction, two new absorption peaks gradually arise at 745 and 570 nm for 1a (745 and 664 nm for 1b). In the oxidation process, new peaks arise at 747 and 593 nm (749 and 595 nm for 1b). These changes are consistent with the spectral changes for other alkylated Pc₂Lu compounds.^[18] Spectroelectrochemistry of a neat film of 1a was also performed in aqueous tetrabutylammonium chloride (TBACI) solution. The UV-vis spectra during the first reduction from the neutral form were monitored under applied potential at -0.6 V vs. reference electrode Ag/AgCI/KCI (Figure 3d). The spectral change followed the same trend as that in solution. The main peak of λ_{max} = 699 nm decreases, and two new peaks increase at 744 and 661 nm. These processes were much faster compared to those in solution due to the limited electrochemically active diffusion layer in the neat film. The oneelectron-reduced species of 1a, which was achieved by immersing a thin film of neutral 1a in an aqueous $Na_2S_2O_4$ reductant solution, was ESR silent (Figure 3a-I).

In summary, we investigated amorphous organic spin-active liquid materials, which differ from the conventional organic spinactive materials that are usually solid due to the π -conjugated parts of the molecules. The embedding of the unpaired electron (spin radical) in the molecule by the bulky and flexible alkyl chains causes it to be well shielded from the environment, as proven by the results of FP-TRMC, ESR, and SQUID measurements. The adopted molecular design can effectively weaken the intermolecular π - π interactions between the Pc₂Lu cores through steric hindrance of the branched long alkyl side chains, and as a consequence, viscous liquids at room temperature can be created. This branched alkyl chain engineering strategy leads to isolation

COMMUNICATION



Figure 3. a) ESR spectra of I) a thin film of one-electron reduced species of 1a, II) a thin film of neutral 1a, III) 1a in dichloromethane (10^{-4} M) , IV) a thin film of neutral 1b, V) 1b in dichloromethane (10^{-4} M) . b) UV-vis spectral changes of a thin film of 1a during the chemical reduction using Na₂S₂O₄ (from red line to blue lines). c) UV-vis spectral changes of 1a in dichloromethane $(2 \times 10^{-5} \text{ M})$ containing 0.1 M of TBAP during the electrochemical reduction at 0 V (red line) and -0.6 V (blue lines). The inset shows a schematic illustration of the environment surrounding the Pc₂Lu molecules. d) UV-vis spectral changes of a thin film of 1a pasted on an ITO working electrode in aqueous TBACI (0.5 M) during the electrochemical reduction at 0 V (red line) and -0.6 V (blue lines). The inset shows a schematic illustration of the environment surrounding the Pc₂Lu molecules.

of the Pc₂Lu core unit in the solvent-free state. Therefore, even the neat film material can maintain the inherent molecular optical, redox, and spin-activities. The shorter branched alkyl chains provided less of the softening effect, but interestingly, affected the solidification process enough to create a supercooled liquid phase. We believe that such π -FMLs with switchable spin- and optical- activities would open up new avenues in soft, fluidic materials that are responsive to multiple stimuli such as magnetic field and redox.

Acknowledgements

This work was partly supported by the Grants-in-Aid for Scientific Research (JSPS KAKENHI Grant Number JP25104011, JP15H03801) from MEXT, Japan. A.Z. is grateful to WUT-NIMS Joint Graduate School Program. The authors thank Dr. T. Taguchi (NIMS) for the use of the rheometer, and Prof. J. Veciana and Dr. M. Mas-Torrent (ICMAB-CSIC) for their

valuable comments on this study. The authors also thank the Soft Materials Line and the MANA TSS Group at NIMS for the use of their facilities.

Conflict of interest

The authors declare no conflict of interest.

Keywords: lutetium double-decker phthalocyanine • functional molecular liquids • supercooled liquid • magnetic properties • electrochromism

- (a) S. S. Babu, T. Nakanishi, *Chem. Commun.* 2013, *49*, 9373–9382;
 (b) A. Ghosh, T. Nakanishi, *Chem. Commun.* 2017, *53*, 10344–10357 and references therein.
- [2] N. Giri, M. G. Del Pópolo, G. Melaugh, R. L. Greenaway, K. Rätzke, T. Koschine, L. Pison, M. F. C. Gomes, A. I. Cooper, S. L. James, *Nature* 2015, 527, 216–220.

COMMUNICATION

- [3] (a) S. S. Babu, J. Aimi, H. Ozawa, N. Shirahata, A. Saeki, S. Seki, A. Ajayaghosh, H. Möhwald, T. Nakanishi, *Angew. Chem. Int. Ed.* 2012, *51*, 3391–3395; (b) S. S. Babu, M. J. Hollamby, J. Aimi, H. Ozawa, A. Saeki, S. Seki, K. Kobayashi, K. Hagiwara, M. Yoshizawa, H. Möhwald, T. Nakanishi, *Nat. Commun.* 2013, *4*, 1969.
- [4] P. Duan, N. Yanai, N. Kimizuka, J. Am. Chem. Soc. 2013, 135, 19056– 19059.
- [5] J.-C. Ribierre, L. Zhao, M. Inoue, P.-O. Schwartz, J.-H. Kim, K. Yoshida, A. S. D. Sandanayaka, H. Nakanotani, L. Mager, S. Méry, C. Adachi, *Chem. Commun.* **2016**, *52*, 3103–3106.
- [6] T. Michinobu, T. Nakanishi, J. P. Hill, M. Funahashi, K. Ariga, J. Am. Chem. Soc. 2006, 128, 10384–10385.
- [7] T. J. Kramer, S. S. Babu, A. Saeki, S. Seki, J. Aimi, T. Nakanishi, J. Mater. Chem. 2012, 22, 22370–22373.
- [8] B. A. Kamino, T. P. Bender, R. A. Klenkler, J. Phys. Chem. Lett. 2012, 3, 1002–1006.
- [9] (a) E. M. Maya, J. S. Shirk, A. W. Snow, G. L. Roberts, *Chem. Commun.* 2001, 615–616; (b) S. Sergeyev, E. Pouzet, O. Debever, J. Levin, J. Gierschner, J. Cornil, R. Gomez Aspe, Y. H. Geerts, *J. Mater. Chem.* 2007, *17*, 1777–1784.
- [10] A. Nowak-Król, D. Gryko, D. T. Gryko, Chem. Asian J. 2010, 5, 904– 909.
- [11] S. Maruyama, K. Sato, H. Iwahashi, Chem. Lett. 2010, 39, 714–716.
- [12] Y. Chino, A. Ghosh, T. Nakanishi, N. Kobayashi, K. Ohta, M. Kimura, *Chem. Lett.* 2017, 46, 1539–1541.
- [13] F. Lu, T. Takaya, K. Iwata, I. Kawamura, A. Saeki, M. Ishii, K. Nagura, T. Nakanishi, *Sci. Rep.* **2017**, *7*, 3416.
- [14] A. Zielinska, M. Leonowicz, H. Li, T. Nakanishi, Curr. Opin. Colloid Interface Sci. 2014, 19, 131–139.
- [15] M. J. Hollamby, M. Karny, P. H. H. Bomans, N. A. J. M. Sommerdijk, A. Saeki, S. Seki, H. Minamikawa, I. Grillo, B. R. Pauw, P. Brown, J. Eastoe, H. Möhwald, T. Nakanishi, *Nat. Chem.* **2014**, *6*, 690–696.
- [16] T. Machida, R. Taniguchi, T. Oura, K. Sada, K. Kokado, *Chem. Commun.* 2017, 53, 2378–2381.
- [17] (a) V. E. Pushkarev, L. G. Tomilova, V. N. Nemykin, *Coord. Chem. Rev.* **2016**, *319*, 110–179 and references therein; (b) K. E. Sekhosana, E. Amuhaya, J. Mack, T. Nyokong, *J. Mater. Chem. C* **2014**, *2*, 5431–5437; (c) W. Zheng, B.-B. Wang, J.-C. Lai, C.-Z. Wan, X.-R. Lu, C.-H. Li, X.-Z. You, *J. Mater. Chem. C* **2015**, *3*, 3072–3080.
- [18] (a) I. Yilmaz, T. Nakanishi, A. Gürek, K. M. Kadish, J. Porphyrins Phthalocyanines 2003, 7, 227–238; (b) K. M. Kadish, T. Nakanishi, A. Gürek, V. Ahsen, I. Yilmaz, J. Phys. Chem. B 2001, 105, 9817–9821.
- [19] M. Maitrot, G. Guillaud, B. Boudjema, J. André, H. Strzelecka, J. R. Simon, Chem. Phys. Lett. 1987, 133, 59–62.
- [20] I. Bidermane, J. Lüder, S. Ahmadi, C. Grazioli, M. Bouvet, B. Brena, N. Mårtensson, C. Puglia, N. Witkowski *J. Phys. Chem. C* 2016, *120*, 14270–14276.
- [21] M. Gonidec, R. Biagi, V. Corradini, F. Moro, V. De Renzi, U. del Pennino, D. Summa, L. Muccioli, C. Zannoni, D. B. Amabilino, J. Veciana, J. Am. Chem. Soc. 2011, 133, 6603–6612.
- [22] (a) A. M. van de Craats, J. M. Warman, H. Hasebe, R. Naito, K. Ohta, J. Phys. Chem. B 1997, 101, 9224–9232; (b) L. F. Li, S.-W. Kang, J. Harden, Q. Sun, X. Zhou, L. Dai, A. Jakli, S. Kumar, Q. Li, Liq. Cryst. 2008, 35, 233–239; (c) Q. Li, Liquid Crystals Beyond Displays: Chemistry, Physics, and Applications, John Wiley & Sons, Hoboken, New Jersey, 2012.
- [23] M Guerbet, C. R. Acad. Sci. 1909, 149, 129–132.
- [24] A. J. O'Lenick Jr., J. Surfactants Deterg. 2001, 4, 311–315.
- [25] M. J. Hollamby, T. Nakanishi, J. Mater. Chem. C 2013, 1, 6178–6183.
- [26] K. Chung, M. S. Kwon, B. M. Leung, A. G. Wong-Foy, M. S. Kim, J. Kim, S. Takayama, J. Gierschner, A. J. Matzger, ACS Cent. Sci. 2015, 1, 94–102.
- [27] K. Ban, K. Nishizawa, K. Ohta, A.M. van de Craats, J. M. Warman, I. Yamamoto, H. Shirai, J. Mater. Chem. 2001, 11, 321–331.
- [28] F. Maeda, K. Hatsusaka, K. Ohta, M. Kimura, J. Mater. Chem. 2003, 13, 243–251.

- [29] T. Komatsu, K. Ohta, T. Fujimoto, I. Yamamoto, J. Mater. Chem. 1994, 4, 533–536.
- [30] T. Komatsu, K. Ohta, T. Watanabe, H. Ikemoto, T. Fujimoto, I. Yamamoto, J. Mater. Chem. 1994, 4, 537–540.
- [31] K. Binnemans, J. Sleven, S. De Feyter, F. C. De Schryver, B. Donnio, D. Guillon, *J. Chem. Mater.* **2003**, *15*, 3930–3938.
- [32] T. Basova, E. Koltsow, A. K. Hassan, A. Nabok, A. K. Ray, A. G. Gurek, V. Ahsan, J. Mater. Sci.: Mater. Electron. 2004, 15, 623–628.
- [33] S. Bistac, M. Brogly in *Handbook of Solvents* (Eds.: G. Wypych), ChemTec Publishing, New York, 2001, pp. 577.
- [34] C. R. Ganivet, B. Ballesteros, G. de la Torre, J. M. Clemente-Juan, E. Coronado, T. Torres, *Chem. - Eur. J.* 2013, *19*, 1457–1465.
- [35] J. Aimi, M. Komura, T. Iyoda, A. Saeki, S. Seki, M. Takeuchi, T. Nakanishi, *J. Mater. Chem. C* 2015, 3, 2484–2490.
- [36] S. Seki, A. Saeki, T. Sakurai, D. Sakamaki, *Phys. Chem. Chem. Phys.* 2014, *16*, 11093–11113.
- [37] A. W. Snow, N. L. Jarvis, J. Am. Chem. Soc. 1984, 106, 4706–4711.
- [38] P. W. Anderson, P. R. Weiss, *Rev. Mod. Phys.* **1953**, *25*, 269–276.
- [39] G. A. Gürek, V. Ahsen, D. Luneau, J. Pecaut, *Inorg. Chem.* 2001, 40, 4793–4797.
- [40] K. L. Trojan, J. L. Kendall, K. D. Kepler, W. E. Hatfield, *Inorg. Chim. Acta* 1992, 795, 198–200.
- [41] C. Piechocki, J. Simon, J.-J. Andre, D. Guillon, P. Petit, A. Skoulios, P. Weber, *Chem. Phys. Lett.* **1985**, *122*, 124–128.

COMMUNICATION

Entry for the Table of Contents

COMMUNICATION

It's fluid now! We created an amorphous and liquid lutetium phthalocyanine (Pc_2Lu). The π -cores of Pc_2Lu are embedded in flexible, bulky, and branched long alkyl chains, and thus shielded well from the environment. The inherent molecular functions of Pc_2Lu , such as spinactive nature and electrochromic behavior are maintained even in the neat liquid state at room temperature.



A. Zielinska, A. Takai, H. Sakurai, A. Saeki, M. Leonowicz, T. Nakanishi*

Page No. – Page No.

A Spin-Active, Electrochromic, Solvent-Free Molecular Liquid Based on Double-Decker Lutetium Phthalocyanine Bearing Long Branched Alkyl Chains