Fully Conjugated Porphyrin Glass: Collective Light-Harvesting Antenna for Near-Infrared Fluorescence beyond 1 μm

Mitsuhiko Morisue,*†‡ Shun Omagari,*§ Ikuya Ueno,† Takayuki Nakanishi,*§ Yasuchika Hasegawa,*§ Shunsuke Yamamoto,*§ Jun Matsui,*§ Sono Sasaki,*§ Takaaki Hikima,*§ and Shinichi Sakurai*§

†Faculty of Molecular Chemistry and Engineering and ‡Faculty of Fiber Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan
§Graduate School of Engineering, Hokkaido University, North 13 West 8, Kita-ku, Sapporo 060-8628, Japan
∥Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
¶Department of Science, Yamagata University, Kojirakawa-cho, Yamagata 990-8560, Japan
§RIKEN SPring-8 Center, 1-1-1, Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5148, Japan

ABSTRACT: Expanded π-systems with a narrow highest occupied molecular orbital—lowest unoccupied molecular orbital band gap encounter deactivation of excitons due to the “energy gap law” and undesired aggregation. This dilemma generally thwarts the near-infrared (NIR) luminescence of organic π-systems. A sophisticated cofacially stacked π-system is known to involve exponentially tailed disorder, which displays exceptionally red-shifted fluorescence even as only a marginal emission component. Enhancement of the tail-state fluorescence might be advantageous to achieve NIR photoluminescence with an expected collective light-harvesting antenna effect as follows: (i) efficient light-harvesting capacity due to intense electronic absorption, (ii) a long-distance exciton migration into the tail state based on a high spatial density of the chromophore site, and (iii) substantial transmission of NIR emission to circumvent the inner filter effect. Suppression of aggregation-induced quenching of fluorescence could realize collective light-harvesting antenna for NIR-luminescence materials. This study discloses an enhanced tail-state NIR fluorescence of a self-standing porphyrin film at 1138 nm with a moderate quantum efficiency based on a fully π-conjugated porphyrin that adopts an amorphous form, called “porphyrin glass”.

INTRODUCTION

There is a growing fascination with near-infrared (NIR) photoluminescent materials aiming at potential applications in a wide range of fields along with the availability of the semiconductor, indium gallium arsenide (InGaAs), to detect NIR light longer than 1 μm, namely, in the shortwave infrared (SWIR) region.1−3 A narrow highest occupied molecular orbital—lowest unoccupied molecular orbital band gap is indispensable to NIR photoluminescence. Among them, fully π-conjugated low-band-gap polymers have hitherto been a pivotal subject in organic photovoltaic applications because NIR light-harvesting capacity has a crucial role in photovoltaic efficiency.4−7 However, narrow energy gaps are intrinsically prone to fast deactivation, known as the “energy gap law”.8,9 Additionally, the expansion of π-conjugated systems is usually accompanied by a drawback arising from the propensity for π-stacking. These bottlenecks make the design of bright NIR photoluminescent chromophores and polymers highly challenging. Actually, lowering the band gap of π-conjugated polymers is not always effective in shifting the emission wavelength to the red unlike the absorption band; poor emission efficiency of some narrow-band-gap polymers apparently violates Kasha’s law,10−13 although that defines the fluorescence as radiative decay from the lowest optical absorption band.14 To overcome the intrinsic inefficiency of NIR/SWIR emission, high excitation efficiency should ensure the brightness of the emission, considering the fact that brightness of emission is defined as the product of light absorption efficiency and emission quantum yield. In this consequence, a strongly light-absorbing material is a possible candidate to yield bright NIR/SWIR emission, even if the emission quantum yield remains inefficient.

A greater absorption band enhances not only efficient light-harvesting capacity but also the inner filter effect in which...
fluorescence is usually reabsorbed, thus reducing the emission intensity. A large Stokes shift of the emission should increase only the light-harvesting antenna effect by circumventing the inner filter effect. It is known that the structural distribution of chromophore assemblies is the sum of Gaussian statistics and tail states, such as exponential tail\textsuperscript{15,16} or heavy-tailed Lévy distributions (Scheme 1 and Figure 1).\textsuperscript{17–21} Although the tail states display only a marginal fluorescence component, enhanced tail-state fluorescence might be a rational strategy to obtain effective NIR/SWIR emission. We envisioned that bulk chromophore aggregates could evolve the emission wavelength up to the lowest edge of the electronic absorption band through enhanced exciton funneling efficiency. Accordingly, only the tail-state fluorescence could be substantially obtained. From this point of view, bulk chromophore assemblies may be intriguing as NIR/SWIR luminescent materials.

Our approach to achieving NIR photoluminescent materials involves imparting a glassy nature to zinc porphyrin by accommodation with two 3,4,5-tri((S)-3,7-dimethyloctyloxy)-phenyl groups at the meso-positions, called “porphyrin glass” in this study.\textsuperscript{22} Molecular glasses or amorphous molecular materials have introduced an excellent morphological strategy in organic optoelectronic devices based on small molecules and polymers.\textsuperscript{23–26} The porphyrin glass is highly resistant to crystallization and is tolerant of expansion of the π-system through supramolecular and covalent polymerization.\textsuperscript{27,28} In principle, the amorphous or glass phase is kinetically constrained from crystallization and incorporates a free volume in the frozen liquid by losing macroscopic fluidity. Thus, the free volume allows some extent of microscopic conformational fluctuation in the photoexcited state, leading to excimer formation. Consequently, the glassy butadiynylene-bridged porphyrin dimer formed the excimer and exhibited solid-state NIR photoluminescence at approximately 970 nm with submicrosecond time constants,\textsuperscript{22} and further expansion of stacked π-systems through supramolecular polymerization achieved SWIR photoluminescence at approximately 1 μm with microsecond decay time constants.\textsuperscript{27} In contrast to a thermodynamically preferable supramolecular polymer structure due to the reversible backbone formation, the covalently linked polymer backbone likely entraps kinetically preferable states. Encouraged by the fact that no aggregation-caused fluorescence quench occurred in porphyrin glass, we explored the NIR/SWIR fluorescence properties of the covalent polymer of the porphyrin glass, expecting the increased probability of the formation of the tail states in bulk.
Oligomeric conjugated porphyrin arrays demonstrate excellent NIR fluorescence in organic solutions,55,50 where the meso-ethylenylene conjugation is a privileged motif of excellent π-electronic features, as established by Anderson et al.31–34 and Therien et al.29,35–39 To date, π-conjugation engineering of meso-ethylenylene porphyrin arrays has been extended to fully conjugated polymers.50–54 However, the porphyrin-conjugated polymers possess a drawback arising from large π-systems, such as undesired aggregation. Featuring an intrinsically glass-forming porphyrin unit, the “molecular wire effect” could be effective in incorporating a light-harvesting antenna function,53–56 in a manner similar to the supramolecular polymer of porphyrin glass.57 Our present objective focuses on a covalently linked polymer glass with a fully π-conjugated backbone.

One of the most efficient π-conjugations of aryl-bridged ethynyl-conjugated porphyrin dimers has been achieved by a possible resonance between a benzenoid–acylene and quinoidal–cumulenic conjugation. This approach was proposed by Anderson and co-workers using a 9,10-anthracene-bridged ethynyl-conjugated porphyrin dimer for the first time57–59 and has been reported for other aryl-bridges such as thiophene,60 pentacene,61 benzothiadiazole,62 dimethylthiazolodiquinoxaline,61 and dithienometallole.63 However, further extension to an alternating anthracene–porphyrin polymer has not been conducted. Along with the study of porphyrin glass, we recently reported an alternating anthracene–porphyrin polymer 1 (Mn = 54 000, Mw/Mn = 4.2, Tg = 94 °C) that formed a metal-lustrous self-standing film, “porphyrin foil” (Figure 2).28 Polymer 1 exhibited a remarkably red-shifted Q band at 904 nm, together with a high refractive index, as an outcome of the considerable persistence length of the π-conjugated backbone.63,64 Compared with a newly synthesized model compound 2, this study discusses an SWIR fluorescent system based on the collective light-harvesting antenna effect of the porphyrin foil.

## RESULTS AND DISCUSSION

### NIR Emission Behaviors in Solution

Polymer 1 exhibited an exceptionally long Q band at 904 nm, whose intensity was unusually stronger than that of the Soret band at 438–543 nm (Figure 3A). In principle, the Q band of porphyrin is optically only partially allowed, and therefore the Q band is usually much weaker than the Soret band.31 To the best of our knowledge, an unusually intense Q band was not reported except for a few exceptions: butadine-linked octaethylporphyrin array65–67 and the meso-ethylenylene-conjugated porphyrin array with an alternating pyrido[3,4-b]pyrazine-zinc porphyrin sequence45 other than a supramolecular polymer of the porphyrin glass in our previous study.27 The intense and red-shifted Q band should be an outcome of the increased π-conjugation.

Extended π-system often causes undesired aggregation even under dilute conditions. The addition of an axial ligand is effective in the dissociation of stacked zinc porphyrins. The addition of pyridine to 1 gave rise to a blue shift of the Q band from 904 to 885 nm with remarkable sharpening, although the emission maxima shifted to the red (Figure 3A). The observed spectral change was unusual, considering that axial coordination typically resulted in a red-shift of the Q band. Actually, a titration experiment of model compound 2 with pyridine resulted in a small red-shift of both the Soret bands at approximately 440 and 530 nm, of the Q bands from 690 to 710 nm, and fluorescence maxima (Figure 4), where the electronic structures were relevant to the reported homologue.57 The spectral change through several pseudo-isosbestic and isoemissive points and the estimated binding strength indicated that 2 was substantially free from aggregation under the experimental conditions. Comparison with the electronic structure of 2 emphasizes the exceptionally sharp Q band of 1 in the presence of pyridine together with the extended π-conjugation. The band width of the Q band, which mirrors the torsional conformations around the ethynylene linkage, was reminiscent of that of the conjugated porphyrin array with all of the units fully planar,32,34 suggesting a narrow conformational distribution. Considering the very low torsional barrier around the ethynylene linkage,68 the 3,4,5-tri((S)-3,7-dimethyloctyloxy)phenyl groups may enhance the geometrical complementarity of π-stacked interactions, similar to the π-stacked porphyrin arrays even in the presence of pyridine.65–67 We consider that a higher molecular weight component of polymer 1 could provide a π-stacked and/or entangled structure. We discuss the electronic properties of polymer 1 in the absence of pyridine to directly compare the photo-electronic properties in solution with those in a pyridine-free amorphous phase.

Photoluminescence properties of polymer 1 were different from those of Kasha’s law14 at a glance. Polymer 1 showed a relatively strong emission at 827 nm, together with a weak emission at 944 nm (Figure 3B), whose emission lifetime was ranged in the time scale of fluorescence. It should be noticed
that the principal emission at 827 nm was attributed to the energy level at 1.53 eV (809 nm as the midpoint of the deconvoluted absorption maximum and emission maximum), higher than the lowest excited state at 1.34 eV (929 nm as the midpoint of the deconvoluted absorption maximum and the longer emission maximum) (Figure 5). The fluorescence maximum at 827 nm was much longer than that of 2 at 743 nm in toluene, indicating that the energy level of the fluorescent species of 1 is lower than that of the π-conjugated domain of a porphyrin−anthracene−porphyrin unit.

A similar fluorescence behavior is known for low-band-gap polymers, such as poly{benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl}{3-fluorothieno[3,4-b]thiophenediyld}, called "PYB7" it has one of the most excellent properties for photovoltaic applications, exhibiting fluorescence at a shorter wavelength than the longest absorption band. This effect is attributed to the folded structure. To access the fluorescence properties, the excitation spectra (Figure 3B) were compared with the deconvoluted electronic absorption spectrum (Figure 5). The distinctive difference of the longer emission at 944 nm from the shorter emission at 827 nm was the greater contribution of the excitation at 543 nm. Additionally, the emission efficiency at 944 nm was very low when the longest Q band at 909 nm was excited. Then, the entire observations may be interpreted in a manner similar to the case of PYB7; photoexcitation of polymer 1 produced two distinct states, that is, a localized exciton on an isolated shorter chain and a relatively delocalized exciton on the stacked or entangled longer chain. The lowest level at 1.34 eV may be prone to deactivation according to the energy gap law, thus dissipating the exciton to reduce the emission efficiency at 944 nm. In solution, exciton funneling from the localized state to the delocalized state may be ineffective due to their large spatial separation between energy-donating and energy-accepting sites, where the Förster critical radius governs the distance of exciton migration. Thus, the shorter emission band at 827 nm was relatively conspicuous. The rational mechanism for the fluorescence behaviors of 1 in toluene is proposed in Figure 5.

The above explanation for the complicated fluorescence behavior of polymer 1 assumes partial aggregation or entanglement of the polymer backbone depending on molecular weight. A spin-cast film of 2 prepared from toluene solution would provide aggregates, whose fluorescence behavior could provide fruitful insights into the fluorescence properties of polymer 1. The spin-cast film of 2 showed a split Q band at 680 and 770 nm and the finely structured Soret band at 443 and 537 nm due to exciton coupling (Figure 6), unambiguously.
indicating partial aggregation. The emission of the spin-cast film at 958 nm showed remarkably large Stokes shift, suggesting excimer formation. The close similarity of the emission wavelength of the spin-cast film of 2 at 958 nm and the solution of 1 at 944 nm may indicate structural resemblance of the emission species.

**Solid-State SWIR Photoluminescence.** In the second stage, our attention was focused on the porphyrin foil of 1, a bulk self-standing neat film approximately 160 μm in thickness (Figure 2C). In the porphyrin foil, 1 adopted a form of amorphous phase at room temperature. The porphyrin foil exhibited emission at 1138 and 950 nm (Figure 7). In this case, the considerable overlap of intense absorption of the porphyrin foil should distort the spectral shape in the wavelength region shorter than the Q band and the normal emission should partly emerge at 950 nm, although the SWIR emission longer than the Q band and the normal emission should partly overlap. Foil should distort the spectral shape in the wavelength region shorter than the Q band and the normal emission should partly overlap. Foil should distort the spectral shape in the wavelength region shorter than the Q band and the normal emission should partly overlap. Foil should distort the spectral shape in the wavelength region shorter than the Q band and the normal emission should partly overlap. Foil should distort the spectral shape in the wavelength region shorter than the Q band and the normal emission should partly overlap. Foil should distort the spectral shape in the wavelength region shorter than the Q band and the normal emission should partly overlap.

![Figure 7. Emission—excitation contour map of the porphyrin foil. Excitation spectrum monitored at 1000 nm (black line), absorption spectrum obtained by spectroscopic ellipsometry (gray line, adapted from ref 28) (left panel), and emission spectra obtained by excitation at 470 and 800 nm (upper panel). It should be noticed that no emission at 827 nm was found.](image)

The spectral shape showed no excitation wavelength dependence (Figure 7), unlike the fluorescence properties in toluene. This fact provides direct evidence that the energy conversion efficiency to the lowest level was unity irrespective of the initial photoexcited level. In the porphyrin foil, the close proximity of the fully conjugated porphyrin arrays should be appropriate for enhancing interchromophore Coulombic coupling for efficient exciton funneling to the lowest energy trap. Although the inner filter effect should also involve trivial energy transfer through emission/re-excitation processes, the contribution should be insignificant considering substantial fluorescence quantum yield.

On the contrary, the spin-cast film of 1 exhibited very faint fluorescence, whose SWIR component was only marginal (Figure S4; details described in the Supporting Information). The collective light-harvesting antenna effect shifted the emission wavelength up to the lowest edge of the electronic absorption band and produced SWIR luminescence.

The emission lifetime measurements of the porphyrin foil revealed that the emission at 1138 nm decayed within a subnanosecond time scale (Figure S3), elucidating that the SWIR emission was definitively in the time range of fluorescence, in contrast with the unusually long emission lifetime of the solid-state NIR/SWIR photoluminescence of previous porphyrin glasses. Therefore, the SWIR fluorescence was likely assigned to the radiative process from the self-trapped exciton at the tail state. The interpretation is most pertinent to the SWIR fluorescence of the porphyrin foil, as represented in Figure 8.

![Figure 8. Possible Jablonski diagram, combined with the electronic absorption spectrum in toluene (yellow) and the fluorescence spectrum of porphyrin foil (red).](image)
Our previous study revealed that the 3,4,5-tri((S)-3,7-dimethyloctyloxy)phenyl groups segregate to the outer surface and reduce the surface free energy of the porphyrin foil.²⁸ Judging from these results, the polymer chains confined by the surface differentiated from the bulk.
The population of the tail state should be minor and unobservable by GIWAXD measurements. In this context, the GIWAXD peaks observed the structures that acted as the light-harvesting antenna. We propose possible structures based on the geometry-optimized model for the WAXD peaks (Figure 10). The anthracene bridging unit of 1 produces a space to stack with the porphyrin ring on the juxtaposed backbone, and the interdigitation of 3,4,5-tri((S)-3,7-dimethyloctyloxy)phenyl groups provides a π-stacked structure with a longitudinal displacement (Figure 10A). The structure is consistent with Bragg’s reflections for the interchain Zn···Zn distances of 10.3 and 8.7 Å as observed at the magnitude of the scattering vector, $q$, of 6.1 and 7.2 nm⁻¹, respectively. The peak found at the $d$-spacing of 16.7 Å implied a nonlinearly ordered backbone with ca. 16.7 Å of the intrachain Zn···Zn spacing (Figure 10B) and overwhelmed the peak of the 18 Å of the intrachain Zn···Zn separation in the π-stacked backbone. Additionally, the broad peak at $q = \text{ca. 14 nm}^{-1}$ was attributed to the halo peak for amorphous alkyl chains, being accompanied by small peaks corresponding to the interchain π-stacked spacing of 3.7 Å. On the contrary, in the GIWAXD pattern measured for the spin-cast film of 1, with rodlike polymer stacking having $d = \text{ca. 30 Å}$, some possible π-stacked structures were observed (Figure 9B).

On the basis of the fact that the SWIR fluorescence quantum yield ranged in a moderate order, these structures did not quench the photoexcited singlet. A slipped-cofacial arrangement of π-stacked porphyrin rings (Figure 10A) could be rational for a long-distance exciton migration because of the close resemblance of the chromophore arrangement in the bacterial light-harvesting antenna complexes.⁶⁸⁻⁷⁰ Of particular importance, the amorphous halo peak at $q = \text{ca. 14 nm}^{-1}$ in the porphyrin foil was more significant than that in the spin-cast film, suggesting that the polymer chain incorporated free volume more as relieving the surface confinement in a bulk. On the basis of this comparison, we interpret that the bulk porphyrin assembly raised the probability of the formation of the tail states.

To ensure photofunctionality under conditions of exceptionally high spatial density of porphyrin rings, an effective morphological strategy featuring porphyrin glass should play a key role in the suppression of undesired aggregation. Therefore, collectively, the light-harvesting antenna function of the porphyrin foil imparted the SWIR with fluorescent properties based on the following factors: (i) an intense electronic absorption band captured the excitation light, (ii) the high spatial density of porphyrin mediated the long-distance exciton migration, and (iii) the substantial transmission of NIR emission circumvented the inner filter effect. The bright SWIR fluorescent site was likely assigned to the tail state, where the plausible structure was the interchain π-stacked structure or the distorted backbone.

---

Figure 9. WAXD profile of the porphyrin foil (red line, adapted from ref 28) and GIWAXD profile of the spin-cast film of the porphyrin array on a silicon wafer (blue line) after background correction (A), where representative peaks are shown as $d$-spacing ($d = 2\pi/q$). The observed GIWAXD pattern (B) and azimuthal-angle dependence of the intensity of the primary GIWAXD peak at the magnitude of the scattering vector, $q$, of approximately 2.1 nm⁻¹ (C).

Figure 10. Geometry-optimized models of the bundle structure of π-stacked chains (blue and red chains) (A), and distorted single backbone (B) produced using an MM+ force field (HyperChem Ver. 8.0 software).
CONCLUSIONS

Considerable absorption by the porphyrin foil showed substantial light-harvesting capacity in the excitation light as well as reabsorption of the fluorescence. The collective light-harvesting capacity efficiently funneled the exciton into the tail state, despite its low population. The exceptional Stokes shift from the absorption band circumvented the inner state, despite its low population. The exceptional Stokes shift highlighted a new methodology to ensure the brightness of the SWIR emission with an inevitably low quantum efficiency. The porphyrin glasses in relatively thermodynamically preferable states, such as porphyrin dimer and supra-molecular polymer, showed excimer-like emission with sub- or microsecond time constants, as shown in our previous study.22,27 By contrast, the covalently linked backbone of the fully conjugated porphyrin glass kinetically entrapped the tail states, wherein the lack of undesired aggregation of the porphyrin rings is of particular importance to accomplish the collective light-harvesting antenna function. The present approach highlighted a new methodology to ensure the brightness of the SWIR emission with an inevitably low quantum efficiency.

EXPERIMENTAL SECTION

Materials. Synthesis of polymer 1 was described in our previous report.26 Model compound 2 was newly synthesized. Synthesis of 2. The model compound 2 was newly synthesized as shown in Scheme 1. To a solution of precursor porphyrin 3 (0.15 g, 87 μmol)65 in diisopropylamine (5 mL) degassed by successive freeze–pump–thaw cycles was added Pd(PPh3)4 (4.8 mg, 4.2 μmol), 9,10-diethynylanthracene (7.5 mg, 29 μmol), and Cul (1.4 mg, 7.4 μmol). The mixture was stirred at 60 °C under argon atmosphere for 15 h and then diluted with toluene to be washed with water. The organic layer was isolated by size-exclusion chromatography (toluene/pyridine, 95:5, v/v). Target compound 2 was obtained as a dark green substance in 5% yield (5.3 mg, 1.5 μmol). 1H NMR (600 MHz, CDCl3): δ 10.05 (d, J = 4.5 Hz, 4H; porphyrin-β), 9.71 (d, J = 4.5 Hz, 4H; porphyrin-β), 9.50 (dd, J = 6.3, 3.3 Hz, 4H; anthranyl), 9.12 (d, J = 4.5 Hz, 4H; porphyrin-β), 8.99 (d, J = 4.5 Hz, 4H; porphyrin-β), 7.96 (dd, J = 6.3, 3.3 Hz, 4H; anthranyl), 7.43 (s, 8H; meso-Ar), 4.45–4.05 (m, 24H; Ar–O–CH2–), 2.19–0.80 (m, 270H; alkyl). 13C NMR (151 MHz, CDCl3): δ 152.7, 152.2, 151.3, 150.5, 150.2, 138.2, 137.1, 133.3, 133.0, 131.3, 131.1, 128.0, 127.4, 123.3, 114.3, 72.1, 67.8, 39.5, 39.3, 37.7, 37.4, 36.6, 30.0, 29.7, 28.1, 27.9, 24.9, 24.7, 22.8, 22.7, 22.6, 19.8, 19.7, 19.1, 12.0. Matrix-assisted laser-dissociation/ionization time-of-flight (MALDI-TOF) mass spectra (dithranol): m/z calc for C224H326N8O12Si2Zn2: 3504.33; found 3504.56 [M]+.

Spectral Methods. NMR spectra were recorded on Bruker AVANCE III 600, and matrix-assisted laser-dissociation/ionization time-of-flight (MALDI-TOF) mass spectra were performed by Bruker Autoflex Speed. Electronic absorption spectra were recorded on a spectrophotometer (UV-1800, SHIMADZU) equipped with a Peltier thermoelectric temperature-controlling unit (TCC-240A, SHIMADZU). The NIR steady-state emission spectra were recorded on a Fluorolog 3 ps NIR spectroscopy system (HORIBA) and corrected for the response of the detector system. Emission lifetimes (τ) of the spin-cast film were measured by nano-LEDs (N-355, response time ≤1.2 ns, HORIBA, Kyoto) and a photomultiplier (RS108, response time ≤1.1 ns, Hamamatsu Photonics, Hamamatsu). Emission lifetimes were determined from the slope of logarithmic plots of the decay profiles. The absolute quantum measurement was performed by QE-5000 (Otsuka Electronics, Osaka) using an integrated sphere equipped with an excitation laser (450 nm). Time-resolved NIR fluorescence was performed by a microscopic UV/IR spectroscopic system (NX-FILM-T03, Tokyo Instruments, Inc.). GIWAXD experiments of the spin-cast film were performed using synchrotron radiation at the BL45XU beamline in SPring-8 (RIKEN SPring-8 Centre Hyogo, Japan) using a PILATUS 3X 2M (Dectris Ltd.) at 308.6 mm of the sample-to-detector distance.71 Resonance Raman spectra were performed by a microscopic spectroscopic Raman spectrometer (HORIBA, LabRAM ARAMIS) by using 532 nm excitation wavelength (Nd:YVO4 laser), wherein the NIR luminescence did not overlap with Raman shift.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00566.

Fluorescence properties of 1 in the presence of pyridine in toluene and the spin-cast film of 1, fluorescence decay profiles, resonance Raman spectrum, spectral data of 2 (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: morisue@kit.ac.jp.

ORCID

Mitsuhiko Morisue: 0000-0002-7783-2492
Takeyuki Nakamishi: 0000-0003-3412-2842
Yasuchika Hasegawa: 0000-0002-6622-8011
Shunsuke Yamamoto: 0000-0002-6854-2477
Jun Matsui: 0000-0003-4767-4507
Shinichi Sakurai: 0000-0002-5756-1066

Present Addresses

1School of Materials and Chemical Technology, Tokyo Institute of Technology, Ookayama 2-12-1-S8, Meguro-ku, Tokyo 152-8552, Japan (S.O.).
2Department of Materials Science and Technology, Tokyo University of Science, 6-3-1 Nijuku, Katsushika-ku, Tokyo 125-8585, Japan (T.N.).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are grateful to Prof. Noriaki Ikeda and Prof. Sadayuki Asaoka (Kyoto Institute of Technology) for fruitful discussion, Mr. Kiminori Etou and Dr. Yoshihiro Osawa (Otsuka Electronics Co., Shiga) for quantum yield measurement, Dr. Hiroyasu Masunaga (Japan Synchrotron Radiation Research Institute, JASRI) and Mr.
Junkyu Park (Kyoto Institute of Technology) for their helpful support during synchrotron X-ray experiments, Tohoku University Material Solutions Center (MaSC) for the time-resolved NIR fluorescence, Kyoto Integrated Science & Technology Bio-Analysis Center (KIST-BIC) for Raman spectroscopic analysis, and Prof. Takuya Nakashima (Nara Institute of Science and Technology) for attempt of magnetic circular dichroism measurements. The synchrotron radiation experiments were performed at BL45XU in SPring-8 with the approval of RIKEN (Proposal No. 20170094). This study was partly supported by KAKENHI (M.M., JP16K05749, J.M., No. 26286010) and KAKENHI (M.M., JP15H00741, J.M., JP15H00720) on the Innovative Area “New Polymeric Materials Based on Element-Blocks (No. 2401)” from JSPS.

REFERENCES

(1) Smith, A. M.; Mancini, M. C.; Nie, S. Second window for in vivo imaging. Nat. Nanotechnol. 2009, 4, 710−711.
(2) Hong, G.; Antaris, A. I.; Dai, H. Near-infrared fluorophores for biomedical imaging. Nat. Biomed. Eng. 2017, 1, No. 0010.
(3) Schnerrmann, M. J. Organic dyes for deep bioimaging. Nature 2017, 551, 176−177.
(4) Liang, Y.; Yu, L. Bulk heterojunction solar cells with exceptionally high performance. Acc. Chem. Res. 2010, 43, 1227−1236.
(5) Dou, L.; Liu, Y.; Hong, Z.; Li, G.; Yang, Y. Low-bandgap near-IR conjugated polymer/polymer for organic electronics. Chem. Rev. 2015, 115, 12633−12655.
(6) Chen, H.-Y.; Hou, J.; Zhang, S.; Liang, Y.; Yang, G.; Yang, Y.; Yu, L.; Wu, Y.; Li, G. Polymer solar cells with enhanced open-circuit voltage and efficiency. Nat. Photonics 2009, 3, 649−653.
(7) Ouyang, X.; Peng, R.; Ai, L.; Zhang, X.; Ge, Z. Efficient polymer solar cells employing a non-conjugated small-molecule electrolyte. Nat. Photonics 2015, 9, 520−524.
(8) Siebrand, W.; Williams, D. F. Radiationless transition in polyatomic molecules. III. Anharmonicity, isotope effects, and single-to-ground-state transition in aromatic hydrocarbons. J. Chem. Phys. 1968, 49, 1860−1871.
(9) Englert, R.; Jortner, J. Multiphoton processes in the Nonradiative decay of large molecules. Mol. Phys. 1970, 18, 145−164.
(10) Tao, M.-M.; Liang, R.; Xing, Y.-D.; Hu, R.; Zhao, N.-J.; Zhang, W.; Fu, L.-M.; Ai, Z.-C.; Zhang, J.-P.; Hou, J.-H. Side-chain effect on the solution-phase conformations and charge photogeneration dynamics of low-bandgap copolymers. J. Chem. Phys. 2013, 139, No. 124094.
(11) Fauvell, T. J.; Zheng, T.; Jackson, N. E.; Ratner, M. A.; Yu, L.; Chen, L. X. Photophysical and morphological implications of single-strand conjugated polymer folding in solution. Chem. Mater. 2016, 28, 2814−2822.
(12) Hedley, G. J.; Steiner, F.; Vogelsang, J.; Lupton, J. M. Determining the true optical bandgap in a high-performance organic photovoltaic polymer using single-molecule spectroscopy. J. Phys. Chem. Lett. 2017, 8, 3494−3499.
(13) Datko, B. D.; Thomas, A. K.; Fei, Z.; Heiney, M.; Grey, J. K. Effect of a heavy heteroatom on triplet formation and interactions in single conjugated polymer molecules and aggregates. Phys. Chem. Chem. Phys. 2017, 19, 28239−28248.
(14) Kasha, M. Characterization of electronic transitions in complex molecules. Discuss. Faraday Soc. 1950, 9, 14−19.
(15) Pope, M.; Sweenberg, C. E. Electronic Processes in Organic Crystals and Polymers; Oxford University Press: New York, 1999.
(16) He, H.; Yu, Q.; Li, H.; Li, J.; Si, J.; Jin, Y.; Wang, N.; Wang, J.; He, J.; Wang, X.; Zhang, Y.; Ye, Z. Exciton localization in solution-processed organolead trihalide perovskites. Nat. Commun. 2016, 7, No. 10896.
(17) Einfeld, A.; Vlaming, S. M.; Malyshew, V. A.; Knoester, J. Excitons in molecular aggregates with Lévy-type disorder: anomalous localization and exchange broadening of optical spectra. Phys. Rev. Lett. 2010, 105, No. 137402.
(18) Vlaming, S. M.; Malyshew, V. A.; Einfeld, A.; Knoester, J. Subdiffusive exciton motion in systems with heavy-tailed disorder. J. Chem. Phys. 2013, 138, No. 214136.
(19) Merda, A.; Jiménez, A. J.; Camacho, K.; Meyer, M.; Würthner, F.; Scheblykin, I. G. Single Lévy State-disorder induced energy funnels in molecular aggregates. Nano Lett. 2014, 14, 6774−6781.
(20) Sorokin, A. V.; Pereverzev, N.; Granika, I. I.; Yefimov, S. L.; Malyavin, Y. V. Evidence of exciton self-trapping in pseudoisocyanine J-aggregates formed in layered polymer films. J. Phys. Chem. C 2015, 119, 27865−27873.
(21) Lüer, L.; Rajendran, S. K.; Stoll, T.; Ganzler, L.; Rebault, J.; Coles, D. M.; Lidzey, D.; Virgili, T.; Cerullo, G. Lévy defects in matrix-immobilized J aggregates: tracing intra-and intersegmental exciton relaxation. J. Phys. Chem. Lett. 2017, 8, 547−552.
(22) Morisue, M.; Ueno, I.; Nakaniishi, T.; Matsui, T.; Sasaki, S.; Matsui, J.; Hasegawa, Y.; Shimizu, M. Amorphous porphyrin glasses exhibit near-infrared excimer luminescence. RSC Adv. 2017, 7, 22679−22683.
(23) Shirotá, Y. Organic materials for electronic and optoelectronic devices. J. Mater. Chem. 2000, 10, 1−25.
(24) Shirotá, Y. Photo- and electroactive amorphous molecular materials: molecular design, syntheses, reactions, properties, and applications. J. Mater. Chem. 2005, 15, 75−93.
(25) Mishra, A.; Bäuerle, P. Small molecule organic semiconductors on the move: promises for future solar energy technology. Angew. Chem., Int. Ed. 2012, 51, 2020−2067.
(26) Grucela-Zajac, M.; Bijak, K.; Kula, S.; Filapek, M.; Waicke, M.; Janecek, H.; Skorka, L.; Gasiorowski, J.; Higerl, K.; Sariciftci, N. S.; Nosidiak, N.; Lewinska, G.; Sanetra, J.; Schab-Balcerzak, E. Photo-physical properties of new molecular glasses end-capped with thiophene rings composed of diimide and imine units. J. Phys. Chem. C 2014, 118, 13070−13086.
(27) Morisue, M.; Hoshino, Y.; Shimizu, M.; Nakaniishi, T.; Hasegawa, Y.; Hossain, M. A.; Sakurai, S.; Sasaki, S.; Uemura, S.; Matsui, J. Supramolecular polymer of near-infrared luminescent porphyrin glass. Macromolecules 2017, 50, 3186−3192.
(28) Morisue, M.; Hoshino, Y.; Shimizu, M.; Tomita, S.; Sasaki, S.; Sakurai, S.; Hikima, T.; Kawamura, A.; Kohri, M.; Matsui, J.; Yamao, T. A metal-lustrious porphyrin foil. Chem. Commun. 2017, 53, 10703−10706.
(29) Duncan, T. V.; Susumu, K.; Sinks, L. E.; Therrien, M. J. Exceptional near-infrared fluorescence quantum yields and excited-state absorptivity of highly conjugated porphyrin arrays. J. Am. Chem. Soc. 2006, 128, 9000−9001.
(30) Pawlicki, M.; Morisue, M.; Davis, N. K. S.; McLean, D. G.; Haley, J. H.; Beauman, E.; Drozbizhev, M.; Rebane, A.; Thompson, A. L.; Pascu, S. I.; Accorsi, G.; Armaroli, N.; Anderson, H. L. Engineering conjugation in para-phenylene-linked porphyrin tapes. Chem. Sci. 2012, 3, 1541−1547.
(31) Anderson, H. L. Building molecular wires from the colours of life: conjugated porphyrin oligomers. Chem. Commun. 1999, 2323−2330.
(32) Anderson, H. L. Conjugated porphyrin ladders. Inorg. Chem. 1994, 33, 972−981.
(33) Taylor, P. N.; Huuskonen, J.; Rumbles, G.; Aplin, R. T.; Williams, E.; Anderson, H. L.; et al. Conjugated porphyrin oligomers from monomer to hexamer. Chem. Commun. 1998, 909−910.
(34) Taylor, P. N.; Anderson, H. L. Cooperative self-assembly of double-stand conjugated porphyrin ladders. J. Am. Chem. Soc. 1999, 121, 11538−11545.
(35) Lin, V. S.-Y.; Therien, M. J. The role of porphyrin-to-porphyrin linkage topology in the extensive modulation of the absorptive and emissive properties of a series of ethynyl- and butadiynyl-bridged bis- and tris(porphyrinato)zinc chromophores. Chem. Eur. J. 1995, 1, 645−651.
(36) Lin, V.; DiMagno, S. G.; Therien, M. J. Highly conjugated, acetylenyl bridged porphyrins: new models for light-harvesting antenna systems. *Science* 1994, 264, 1105–1111.

(37) Kumbel, R.; Palese, S.; Lin, V. S.-Y.; Therien, M. J.; Hochstrasser, R. M. Ultrafast dynamics of highly conjugated porphyrin arrays. *J. Am. Chem. Soc.* 1998, 120, 11489–11498.

(38) Susumu, K.; Therien, M. J. Decoupling optical and photodissociative events in N-carbazole substituted porphyrin-containing organic molecular wires. *Angew. Chem., Int. Ed.* 2013, 52, 12439–12444.

(39) Doria, P.; Von Bargen, C. D.; Olivier, J.-H.; Kumbel, A. S.; Saven, J. G.; Therien, M. J. Single-handed helical wrapping of single-wall carbon nanotubes by chiral, ionic, semiconducting polymers. *J. Am. Chem. Soc.* 2013, 135, 16220–16234.

(40) Anderson, H. L.; Martin, S. J.; Bradley, D. D. C. Synthesis and third-order nonlinear optical properties of a conjugated porphyrin polymer. *Angew. Chem., Int. Ed.* 1994, 33, 655–657.

(41) Kuebler, S. M.; Denning, R. G.; Anderson, H. L. Third-order electronic polarizability of a conjugated porphyrin polymer. *J. Am. Chem. Soc.* 2000, 122, 339–347.

(42) Screen, T. E. O.; Lawton, K. B.; Wilson, G. S.; Dolney, N.; Isaposiou, R.; Goodson, T., III; Martin, S. J.; Bradley, D. D. C.; Anderson, H. L. Synthesis and third order nonlinear optics of a new soluble conjugated porphyrin polymer. *J. Mater. Chem.* 2001, 11, 312–320.

(43) Mróz, M. M.; Lüer, L.; Hourauer-Rassin, C.; Anderson, H. L.; Cabanillas-Gonzalez, J. Role of amorphous and aggregate phases on field-induced exciton dissociation in a conjugated polymer. *Phys. Rev. B* 2013, 87, No. 035201.

(44) Huang, X.; Zhu, C.; Zhang, S.; Li, W.; Guo, Y.; Zhang, X.; Liu, Y.; Bo, Z. Porphyrin-dithienothiophene π-conjugated copolymers: synthesis and their applications in field-effect transistors and solar cells. *Macromolecules* 2008, 41, 6985–6992.

(45) Huang, X.; Shi, Q.; Chen, W.-Q.; Zhu, C.; Zhou, W.; Zhao, Z.; Duan, X.-M.; Zhan, X. Low-bandgap conjugated donor-acceptor copolymers based on porphyrin with strong two-photon absorption. *Macromolecules* 2010, 43, 9620–9626.

(46) Zhou, W.; Jin, F.; Huang, X.; Duan, X.-M.; Zhan, X. A low-bandgap polymer based on porphyrin and dithienocoronene dimide with strong two-photon absorption. *Macromolecules* 2012, 45, 7823–7828.

(47) Jiang, F.-L.; Fortin, D.; Harvey, P. D. Synthesis, characterization, and photophysical properties of conjugated organometallic Pt-acyclicle/Zn(II) porphyrin-containing oligomers. *Inorg. Chem.* 2010, 49, 2614–2623.

(48) Langlois, G.; Aly, S. M.; Gros, C. P.; Barbie, J.-M.; Harvey, P. D. Rational synthetic design of well-defined Pt(bisethylthienyl)/Zn- (porphyrin) oligomers for potential applications in photonics. *New J. Chem.* 2011, 35, 1302–1314.

(49) Wang, X.; Brissard, G.; Fortin, D.; Karsenti, P.-L.; Harvey, P. D. Push-pull porphyrin-containing polymers: materials exhibiting ultrafast near-infrared photophysics. *Macromolecules* 2015, 48, 7024–7038.

(50) Jiang, B.; Yang, S.-W.; Barbini, B. C.; Jones, W. E., Jr. Synthesis of soluble conjugated metalloporphyrin polymers with tunable electronic properties. *Chem. Commun.* 1998, 213–214.

(51) Yamamoto, T.; Fukushima, N.; Nakajima, H.; Maruyama, T.; Yamaguchi, I. Synthesis and chemical properties of π-conjugated zinc porphyrin polymers with arylene and aryleneethynylene groups between zinc porphyrin units. *Macromolecules* 2000, 33, 5988–5994.

(52) Tsai, M.-C.; Wang, C.-L.; Lin, C.-Y.; Tsai, C.-L.; Yen, H.-J.; You, H.-C.; Liou, G.-S. A novel porphyrin-containing polymide for memory devices. *Polym. Chem.* 2016, 7, 2780–2784.

(53) Swager, T. M. The molecular wire approach to sensory signal amplification. *Acc. Chem. Res.* 1998, 31, 201–207.

(54) Rochat, S.; Swager, T. M. Conjugated amplifying polymers for optical sensing applications. *ACS Appl. Mater. Interfaces* 2013, 5, 4488–4502.

(55) Swager, T. M. 50th Anniversary perspective: conductive/semitranslucent conjugated polymers. A personal perspective on the past and the future. *Macromolecules* 2017, 50, 4867–4886.