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Amorphous porphyrin glasses exhibit near-infrared excimer luminescence†

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The amorphous nature of a series of zinc–porphyrins bearing two 3,4,5-tri((*S*)-3,7-dimethyloctyloxy)phenyl groups at the *meso*-positions, named "porphyrin glass", were tolerant of π-conjugation engineering in ethynylene-linked dimers. The butadiyne-linked dimeric porphyrin glass formed an intermolecular excimer, which exhibited bright and exceptionally long-lived, near-infrared (NIR) luminescence at approximately 970 nm in the solid state. Therefore, porphyrin glasses overcame a general bottleneck for NIR-luminescence, such as an undesired π-stacked aggregation of a large porphyrin plane in addition to the energy gap law. The formation of amorphous molecular glasses from a series of *meso*-ethynylene-conjugated zinc–porphyrins, named "porphyrin glass", is described. The butadiyne-linked dimeric porphyrin glass formed an intermolecular excimer, which exhibited solid-state, near-infrared (NIR) luminescence at approximately 970 nm.

Introduction

Metalloporphyrins have been one of the key photofunctional compounds at the forefront of materials science.[1] Near-infrared (NIR) luminescent materials have versatile state-of-the-art applications, in fields such as *in vivo* imaging through the "biological optical window" (800–1350 nm),[2] light-emitting diodes,[3] and broadband optical amplifiers.[4] However, the wavelength of NIR-luminescence of an organic chromophore barely exceeds 900 nm, with only a few exceptions, such as benzothiadiazole derivatives[2d,e,3] and polymethine dyes,[5] as well as porphyrins.[6] An intrinsic obstacle for NIR luminescence comes from the "energy gap law". As an optical band-gap narrows, excitons easily dissipate through thermal perturbation from vibrational oscillations.[7] The *meso*-ethynylene-conjugated porphyrin oligomers exhibit outstanding NIR light-harvesting capacity,[8,9] based not only on intense linear absorption but also on exceptional two-photon absorption cross-section values.[10] The excellent photoelectronic properties of the porphyrins stem from extended *meso*-ethynylene-conjugation, but encounter undesired π-stacked aggregation. Such a drawback prevents the ethynylene-conjugated porphyrins from being used in NIR-luminescence applications under matrix-free conditions.[11] Amorphous glassy molecules have introduced effective and challenging morphological strategies for attaining photoelectronic functionality that is relevant to molecular formulae.[12,13] Hence, *meso*-ethynylene-conjugated porphyrin glasses may be potential NIR-luminescent materials.

The present target is based on our serendipitous discovery that a zinc porphyrin bearing two 3,4,5-tri((*S*)-3,7-dimethyloctyloxy)phenyl groups at the *meso*-positions, such as **1**, adopts the form of a solvent-free viscous fluid at room temperature (Fig. 1).[14] Metallocomplexes, including metalloporphyrins, are usually crystalline and barely form amorphous solids with a few exceptions.[15,16] A deliberate alkylation indicates a potential strategy to provide amorphous molecular glasses. For instance, the introduction of alkyl substituents is crucial for the

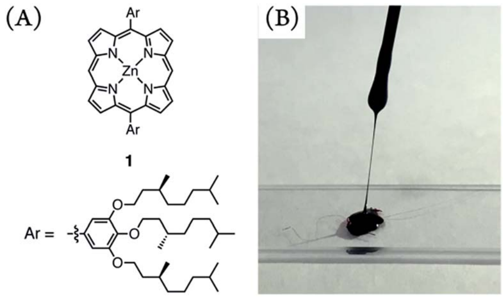

Fig. 1 The chemical structures of porphyrin **1** (A) and a photograph of neat **1** as a sticky fluid on a glass slide at room temperature (B).

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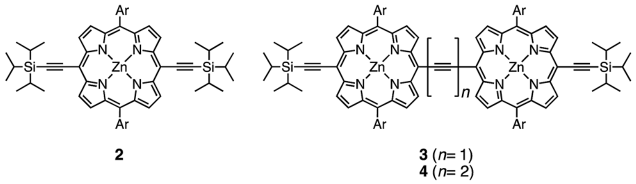
morphology of π-conjugated polymers[17] and nonvolatile fluids.[18,19] Porphyrin fluid **1** prompted us to explore porphyrin glasses with *meso*-ethynylene-conjugations.

Results and discussion

Monomeric porphyrins **1** and **2** showed glass transition temperatures (T_g) at −6 and 19 °C, respectively, in differential scanning calorimetric (DSC) analyses (Scheme 1, Fig. 2), indicating the formation of glass. The results were in sharp contrast with porphyrins incorporating 3,4,5-tri(*n*-alkyloxy)phenyl groups at the *meso*-positions, which crystallize without a glass transition from both liquid and liquid crystalline (LC) states.[19,20] Encouraged by these results, we synthesized **3** and **4** to expand the π-conjugation by connecting two glass-forming porphyrin subunits and aimed to achieve NIR-active porphyrin glasses.

The DSC thermograms of **3** and **4** showed endothermic profiles at 31 °C and 59 °C, respectively, attributed to their glass transitions (Fig. 2), while the others involved enthalpic relaxation. The T_g point shifted to higher temperatures with extended π-conjugations. Porphyrins **1–4** provided neither crystals nor thermotropic LC-phases, even though 3,4,5-tri((*S*)-3,7-dimethyloctyloxy)phenyl groups are known as powerful LC-forming units,[21,22] indicating that the 3,4,5-tri((*S*)-3,7-dimethyloctyloxy) phenyl group is an exquisite partner of porphyrin that encumbers the π-stacked interaction. Further investigations of **2–4** were examined in a uniform thin film prepared by a spin-cast method, as shown below.



Scheme 1 Chemical structures of porphyrin **2** and porphyrin dimers **3** and **4**.

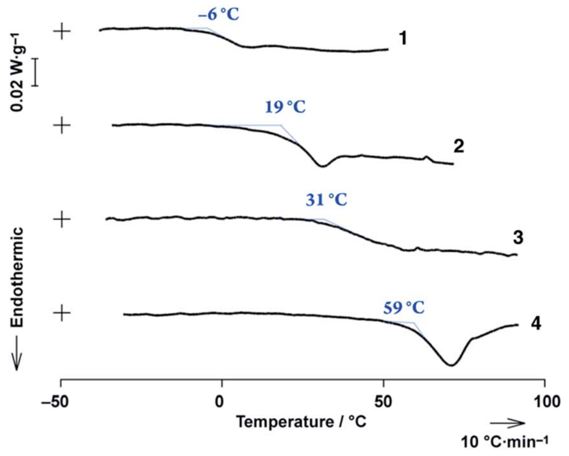


Fig. 2 DSC profiles for **1–4** with a 10 °C min^{-1} heating rate.

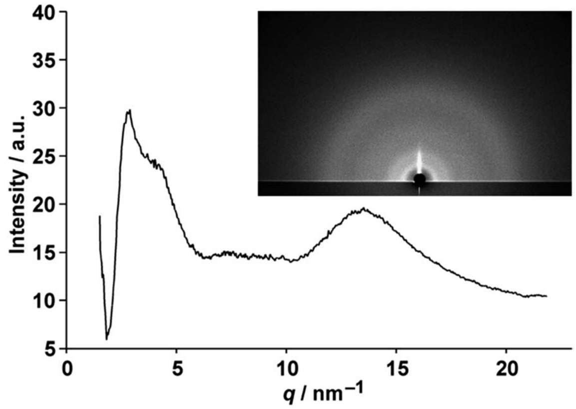


Fig. 3 The GIXS pattern (inset) and one-dimensional profile of **4** on a silicon wafer observed with a synchrotron X-ray with 0.11° of the incident angle obtained from integrated radial azimuthal angles.

Synchrotron microbeam glazing-incidence X-ray scattering (GIXS) found characteristic amorphous halo patterns at approximately a q ($=2\pi/d$, wherein d refers to spacing) of 13.5 nm^{-1} for **2–4** in spin-cast films on a silicon wafer. However, no periodic spacings were found other than primary intramolecular spacing (Fig. 3). Therefore, the blanched alkyl-chains did indeed govern the intermolecular interactions and disordered porphyrin arrangements in solvent-free bulk solid.

Amorphous molecular glass is expected to be persistent to aggregation-caused fluorescence quenching. Remarkably, the porphyrin glass **4** exhibited broad NIR-luminescence at approximately 970 nm that extended to over 1100 nm (Fig. 4), and the monomeric fluorescence was weakened or extinguished instead. Since none of the electronic absorption bands of **4**

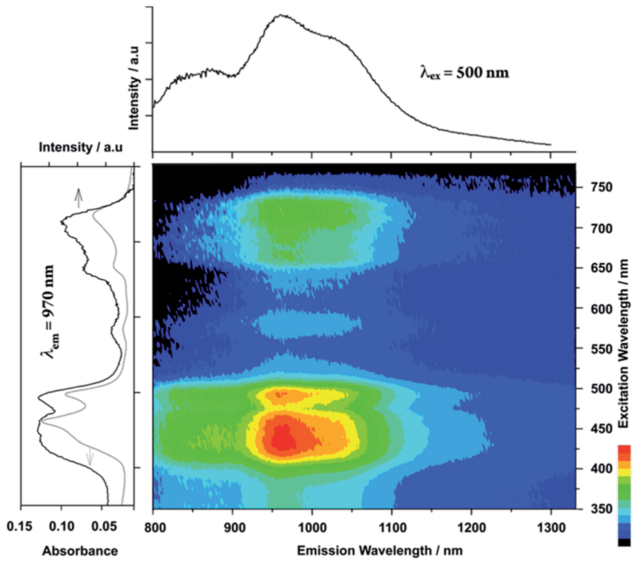


Fig. 4 Emission–excitation correlations of **4** in a spin-cast film on a quartz substrate under air together with an emission spectrum (excitation wavelength = 500 nm) in the upper panel, and excitation (emission wavelength = 970 nm, black line) and absorption (grey line) spectra in the left panel.

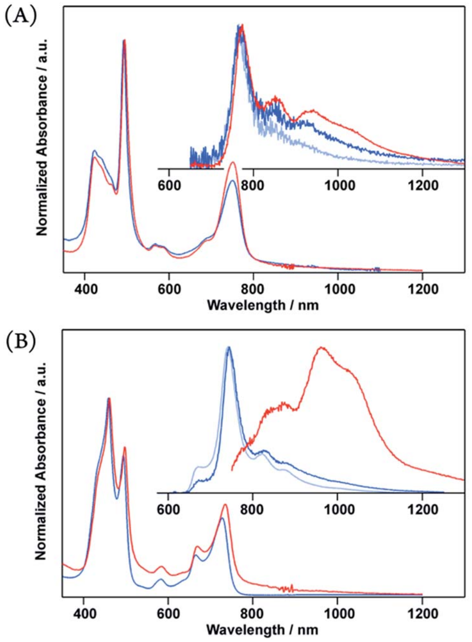


Fig. 5 Normalized absorption and emission spectra of neat porphyrin (red) and porphyrin-doped PMMA (10 wt%, blue, and 1 wt% pale blue) (A: **3**, B: **4**) in spin-cast film on a quartz substrate. Emission obtained by excitation at 500 nm.

exceeded 750 nm, the NIR-luminescence was assigned to the intermolecular excited dimer, *i.e.*, the excimer comprised an excited-state intermolecular chromophore associated with a ground-state counterpart, as elucidated below.

Intermolecular excimer formation was evidenced by the dispersion experiments in an amorphous polymer matrix, where 1 and 10 wt% of **4** were doped into an inert poly(methyl methacrylate) (PMMA) film. In the electronic absorption results, the spectral shape of **4** showed no substantial changes regardless of the fraction of **4** used in the PMMA films (1–100 wt%) (Fig. 5 and S2–S4†), suggesting the occurrence of marginal intermolecular interactions at the ground state in the neat spin-cast film.[23] However, **4**-doped PMMA films showed monomeric emission at 744 nm, and their NIR-luminescence dramatically weakened. The comparison clearly indicates that an intermolecular excimer formation is indispensable for the NIR-luminescence of porphyrin glass.

Excimer formation was predominantly observed only in **4** among the present porphyrin glasses. For example, **2** and **3** mainly showed monomeric fluorescence, which was accompanied by a weak, broad emission at longer wavelengths. It was deduced that an appropriate internal porphyrin–porphyrin separation of **4** opens a space acceptable for intermolecular excimer formation.

It is remarkable that excimers in the porphyrin glasses surpass general obstacles due to the energy gap law.[7] Moreover, large π-systems are prone to undesirable π-stacked aggregations. Thus, NIR-luminescent chromophore aggregates have rarely been reported,[24] and porphyrins have never been the exception. Unlike structureless emissions from excimers in the solution, the solid-state NIR excimer luminescence bears vibronic features (Fig. 6). The vibronic spacing of approximately 1100 cm^{-1} for **3** and 1600 cm^{-1} for **4** were reminiscent of the resonance Raman vibrational modes of the porphyrin skeleton and ethynylene-linkage (Fig. 6),[25] which suggests the presence of exciton–phonon coupling, such as Herzberg–Teller-type dynamic intensity borrowing.[9,26] We propose that the exciton self-traps to resonantly facilitate radiative decay at the excimer site. Therefore, luminescence remains even at NIR wavelengths.

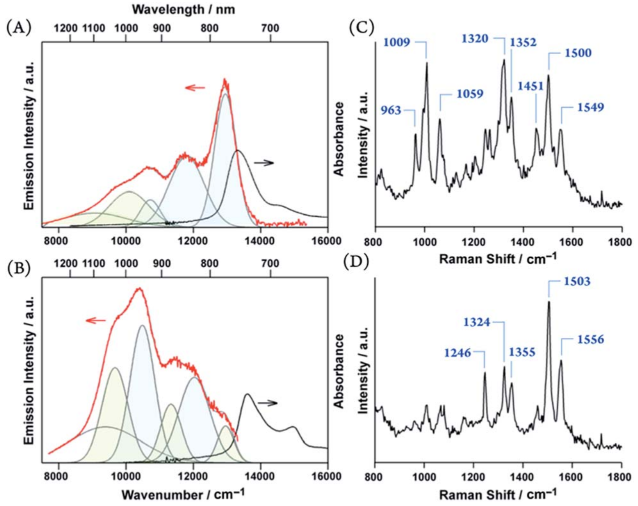


Fig. 6 Emission spectra (red) and electronic absorption (black) (A and B), resonance Raman spectra excited at 532 nm (C and D) of **3** (A and C) and **4** (B and D). Deconvoluted emission peaks with periodic spacings of approximately 1100 cm^{-1} (A) and 1600 cm^{-1} (B) are colored in pale blue and green.

Table 1 NIR luminescence profiles of porphyrin glasses[a]

	770 nm		970 nm		
	$\tau_1(\alpha_1)$/ns	$\tau_2(\alpha_2)$/ns	$\tau_1(\alpha_1)$/ns	$\tau_2(\alpha_2)$/ns	Φ/%
2	240(0.66)	1311(0.34)	76(0.59)	606(0.41)	0.056
3	231(0.66)	1263(0.34)	132(0.66)	953(0.34)	0.039
4	128(0.54)	756(0.46)	103(0.57)	711(0.43)	0.114

[a] Emission lifetime (τ) and normalized pre-exponential factor (α); excitation at 450 nm for **2** and at 500 nm for **3** and **4** (10 wt% **4**-doped PMMA was employed to observe a monomeric component at 770 nm). Tentative emission quantum yield (Φ) was measured for opaque neat drop-cast films by excitation at 450 nm.

All the experiments were performed under aerobic conditions, indicating that the NIR-luminescence was relatively persistent to oxygen. The emission lifetimes of the excimer components were considerably elongated (τ > 500 ns) from the monomeric fluorescence ($\tau \approx$ 100 ns) (Table 1), in contrast to the very short lifetimes reported for the porphyrin films.[27] It was difficult to assign such unusually long-lived luminescence to a singlet exciton, although the photophysical process is the subject under active investigation. The molar extinction coefficient (ε) of **4** displays an exceptional order of 10^5 M^{-1} cm^{-1} both at the Soret and Q bands. The brightness of the emission is defined as the product of the ε value and the absolute quantum yield (Φ).[28] Although the luminescence efficiency ($\Phi = 0.11\%$ as a tentative magnitude) was still comparable to those of the NIR-luminescent polymethine dyes,[5] the excellent ε magnitude of porphyrin glass **4** ensured sufficient brightness of the NIR-luminescence.

Conclusion

In conclusion, we have developed π-conjugated porphyrin glasses. The amorphous nature of the porphyrin glass was highly tolerant of the *meso*-ethynylene π-conjugation engineering. The excimer luminescence of **4** displayed a remarkable Stokes shift toward the NIR-wavelength region presumably through the aid of exciton–phonon coupling. Ethynylene-conjugated porphyrin glasses have highlighted a new fascinating approach towards developing solid-state NIR-luminescent materials. For instance, their amorphous nature was tolerant of further supramolecular π-electron engineering by employing our supramolecular approach[14] toward NIR-luminescence beyond 1000 nm.[29] A further study of NIR-luminescent porphyrin glasses and detailed mechanism of the solid-state NIR-luminescence are currently under active investigation.

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