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((5)-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. 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), light-emitting diodes, and broadband optical amplifiers. However, the wavelength of NIR-luminescence of an organic chromophore barely exceeds 900 nm, with only a few exceptions, such as benzo[a]diazole derivatives and polymethine dyes, as well as porphyrins. 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. The meso-ethynylene-conjugated porphyrin oligomers exhibit outstanding NIR light-harvesting capacity, based not only on intense linear absorption but also on exceptional two-photon absorption cross-section values. 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. Amorphous glassy molecules have introduced effective and challenging morphological strategies for attaining photoelectronic functionality that is relevant to molecular formulae. 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((5)-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). Metallocomplexes, including metalloporphyrins, are usually crystalline and barely form amorphous solids with a few exceptions. 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](image_url)  
(A) 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).
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 \( \text{meso} \)-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 \( \pi \)-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 \( \pi \)-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 \( \pi \)-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.

Synchrotron microbeam glazing-incidence X-ray scattering (GIXS) found characteristic amorphous halo patterns at approximately a \( q \approx 2\pi/d \) (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 intra-molecular 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...
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. Note, however, that 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. Moreover, large π-systems are prone to undesirable π-stacked aggregations. Thus, NIR-luminescent chromophore aggregates have rarely been reported, 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), which suggests the presence of exciton–phonon coupling, such as Herzberg–Teller-type dynamic intensity borrowing. We propose that the exciton self-traps to resonantly facilitate radiative decay at the excimer site. Therefore, luminescence remains even at NIR wavelengths.

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 (τ ≈ 100 ns) (Table 1), in contrast to the very short lifetimes reported for the porphyrin films. 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

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**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.

**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\(^a\)

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<thead>
<tr>
<th></th>
<th>770 nm</th>
<th>970 nm</th>
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<tr>
<td></td>
<td>τ(_1)(s)/ns</td>
<td>τ(_2)(s)/ns</td>
</tr>
<tr>
<td>2</td>
<td>240(0.66)</td>
<td>1311(0.34)</td>
</tr>
<tr>
<td>3</td>
<td>231(0.66)</td>
<td>1263(0.34)</td>
</tr>
<tr>
<td>4</td>
<td>128(0.34)</td>
<td>756(0.46)</td>
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\(^a\) Emission lifetime (τ) and normalized pre-exponential factor (a); 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.
at the Soret and Q bands. The brightness of the emission is defined as the product of the $\epsilon$ value and the absolute quantum yield ($\Phi$). Although the luminescence efficiency ($\Phi = 0.11\%$ as a tentative magnitude) was still comparable to those of the NIR-luminescent polymethine dyes, the excellent $\epsilon$ magnitude of porphyrin glass 4 ensured sufficient brightness of the NIR-luminescence.

**Conclusion**

In conclusion, we have developed $\pi$-conjugated porphyrin glasses. The amorphous nature of the porphyrin glass was highly tolerant of the glasses. The amorphous nature of the porphyrin glass was still comparable to those of the NIR-luminescent porphyrin glasses and detailed mechanism of the luminescence.

**Notes and references**


