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Convenient Synthesis of a Highly Soluble and Stable Phosphorescent Platinum Porphyrin Dye

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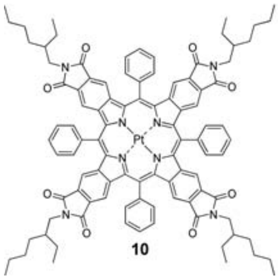
ABSTRACT



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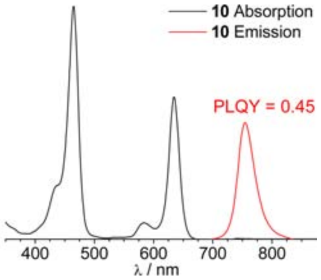

A new highly soluble platinum porphyrin derivative 10 with suppressed photobleaching is prepared on a multigram scale from inexpensive starting materials. 10 possesses intense absorption bands at λ = 463 nm (log ε = 5.39) and 633 nm (log ε = 5.20) with near-IR emission at 755 nm. Efficient NIR phosphorescence (PLQY = 0.45) and a large Stokes shift (eliminating self-absorption) make it an attractive and readily available material for a number of applications.

Owing to their exceptionally strong light absorption and other optoelectronic properties brought about by an extended π-electron system, porphyrins have found widespread applications as optoelectronic and photonic materials. These include optical limiters,[1] nonlinear optics,[2] and dye-sensitized solar cells[3] as well as bioimaging[4] and photodynamic therapy.[5] Their optical, electronic, and even magnetic properties can be widely tuned by extending the conjugation on the pyrrole moiety and by coordination to different metals. Thus, an efficient intersystem crossing and low triplet energy in platinum porphyrinoids make them important phosphorescent dyes. In fact, platinum octaethylporphyrin (PtOEP) was the first material used in phosphorescent light-emitting diodes.[6]

Extending the π-conjugation by fusing additional aromatic rings in the β-position of pyrrole moieties (as in tetrabenzoporphyrins, TBP, and tetranaphthoporphyrins, TNP) leads to a significant bathochromic shift of the absorption/emission properties[7] yielding an important class of near-infrared (NIR) dyes. Their emission can be even further red-shifted through heavy metal coordination (e.g., platinum) to promote intersystem crossing ($S_1 \rightarrow T_1$) and subsequent phosphorescence ($T_1 \rightarrow S_0$).[8] Thus, an efficient near-IR emission with extremely low self-absorption demonstrated by platinum tetraphenyltetrabenzoporphyrin (PtTPTBP) was the key enabling a breakthrough in performance for luminescent light concentrators.[9]

However, planar rigid molecules such as TBP and TNP suffer from vanishingly low solubility, unless functionalized

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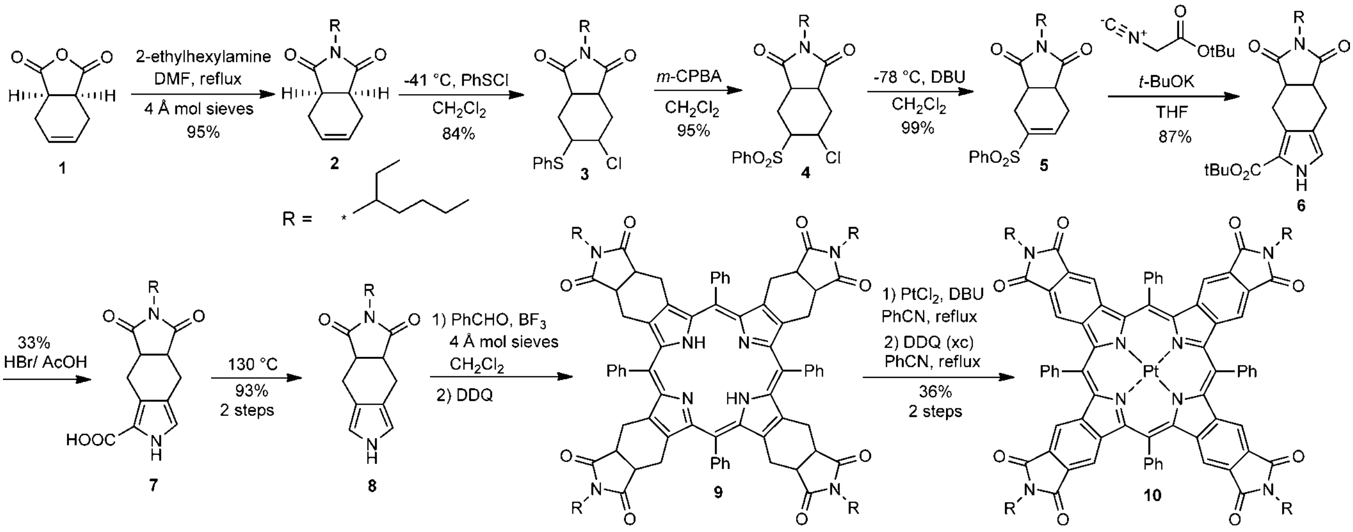
Scheme 1. Synthesis of Platinum Porphyrin **10**



with solubilizing groups.[10] This limits their photophysical studies and hampers their use in applications requiring solvent processing. Despite widespread interest in these materials, the scaled-up preparation of TBPs remains one of significant synthetic effort and tedious purification. Most published TBP synthetic procedures are performed on the milligram scale, which limits the application of these compounds in materials science and other fields. The synthetic challenges for TBP systems reside in the instability of the benzo[c]pyrrole (isoindole) precursor. The practical assembly of the TBP system can proceed through one of the two main pathways:[11] cyclization of tetrahydroisoindole derivatives with subsequent oxidative aromatization[12] or the retro-Diels–Alder formation[13] of the benzo[*c*]pyrrole moiety after the assembly of the porphyrin ring. The latter method has the advantage of quantitative conversion of a soluble precursor porphyrin to TBP, but the former method, developed by Vinogradov and co-workers[12] and used in this work, is of a broader synthetic scope.

Our interest in TBPs has been to design molecular materials for use in solar concentrators. Accordingly, the target tetrabenzoporphyrin **10** was designed to address solubility, photostability, and luminescent properties. The cyclic imide moiety and the branched 2-ethylhexyl group were introduced to minimize oxidative degradation (via lowering the HOMO) and to improve the solubility, respectively.

Condensation of 2-ethylhexylamine and *cis*-1,2,3,6-tetrahydrophthalic anhydride **1** (two low-cost compounds, ~$50/kg) resulted in imide **2** (Scheme 1). Its subsequent chlorosulfanylation, oxidation of phenylsulfane **3** into sulfone **4**, and DBU-promoted dehydrochlorination yielded sulfonylcyclohexene **5** as described earlier for other cyclohexene derivatives.[14] Barton–Zard condensation of phenylsulfone **5** using *tert*-butyl isocyanoacetate afforded the *tert*-butyl ester **6** in high yields as an amorphous solid (86%). Condensation was also performed using ethyl isocyanoacetate, but subsequent conversion to the tetrahydroisoindole **8** failed due to unexpected imide hydrolysis under both acidic and basic conditions. Ester **6** can be easily prepared in > 100 g batches (65% overall yield from **1**) and is a convenient stable intermediate in the synthesis.

Treatment of **6** with 33% HBr in acetic acid resulted in de-esterification and partial decarboxylation, yielding a crude mixture of **7** and **8** (9:1, according to ^{1}H NMR). Heating this mixture at 130 °C for 45 min completed the decarboxylation and afforded tetrahydroisoindole **8** in a good yield (93%). We note that **8** displayed limited stability in air and should be either used immediately or stored under nitrogen at −20 °C. Oxidative polycondensation of **8** with benzaldehyde, according to the Lindsey method,[15] was used to assemble the porphyrin ring **9**. The crude porphyrin **9** can be used in the following step without purification. Platinum insertion and aromatization was accomplished in a one-pot reaction by refluxing **9** in PhCN[16] with $PtCl_2$ followed by addition of DDQ. All synthetic steps can be conveniently carried out on large scales, and we have prepared 2.35 g of **10** in one batch in 36% yield (for **8** → **10** step; 22% overall yield from **1**). The preparation of **10** can be further scaled up although our

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[16] Lower-boiling solvents such as CH_3CN or PhMe were unsuccessful in completely aromatizing the tetrahydroisoindole rings.

initial attempt producing a 7 g batch of **10** suffered a lower yield[17] (15% for **8** → **10**).

Porphyrin **10** is obtained as a dark green flaky powder melting at 363 °C and is soluble in most organic solvents. To our knowledge, solubility values for TBP derivatives have not been reported in literature. Saturated solutions of **10** in various solvents were prepared, and molar solubility values were determined spectroscopically (Table 1).

Table 1. Solution Saturation Points of **10** in Organic Solvents at Room Temperature with Corresponding Absorption Maxima

		solubility		λ_{max}/nm (log(ε))	
solvent	$E_T(30)$	g/L	mol/L	Soret	Q-band
CH_3OH	55.4	0.12	7.0×10^{-5}	462 (5.11)	632 (4.89)
CH_3CN	45.6	0.65	3.8×10^{-4}	461 (5.26)	631 (5.02)
CH_2Cl_2	40.7	400	0.23	464 (5.39)	634 (5.20)
THF	37.4	510	0.30	461 (5.35)	631 (5.14)
$PhCH_3$	33.9	600	0.35	463 (5.37)	633 (5.19)
hexanes	31	2.2	1.3×10^{3}	457 (5.36)	628 (5.23)

As might be expected from the structure of **10** (polarizable aromatic core and aliphatic chains), it shows the greatest solubility in medium polarity solvents. The achieved exceptionally high solubility, up to 600 g/L, can be attributed to the four branched 2-ethylhexyl chains with stereogenic centers and the meso-phenyl substituents reducing the planarity for **10**.

Remarkably, although **10** should exist as a statistical mixture of six stereoisomers, slow evaporation of its solution in a benzene/methanol/chloroform mixture produced a single crystal of the pure (*R*,*S*,*R*,*S*)-**10** (Figure 1). Its X-ray analysis reveals a saddle-shape conformation, typical for related TPTBPs.[18] NSD analysis[19] revealed **10** to have a relatively low out-of-plane distortion (D_{oop} = 2.27 Å compared to 2.83 Å for PtTPTBP[20]) almost completely described by the B_{2u} mode (2.24 Å) associated with saddling. This could be a result of the depleted electron density on CH bonds of the benzopyrrole moiety reducing the repulsion with the phenyl rings.

Cyclic voltammetry of **10** in CH_2Cl_2 reveals two reversible single-electron reductions ($E_{1/2}{}^{1red}$ = −1.36 V and $E_{1/2}{}^{2red}$ = −1.65 V, vs Fc/Fc^+) and one reversible single-electron oxidation wave ($E_{1/2}{}^{1ox}$ = 0.67 V) (Figure 2). The 0.36 V positive shift of $E_{1/2}{}^{1ox}$ compared to $Pt(PhCO_2Me)_4$-TBP[20] indicates a significantly lowered HOMO and suggests an improved oxidation stability. A similar HOMO stabilization in platinum TBP derivatives was previously achieved by incorporating 12 electron-withdrawing methoxycarbonyl substituents ($E_{1/2}{}^{1ox}$ = 0.70 V, $E_{1/2}{}^{1red}$ = −1.36 V, vs Fc/Fc^+).[21]

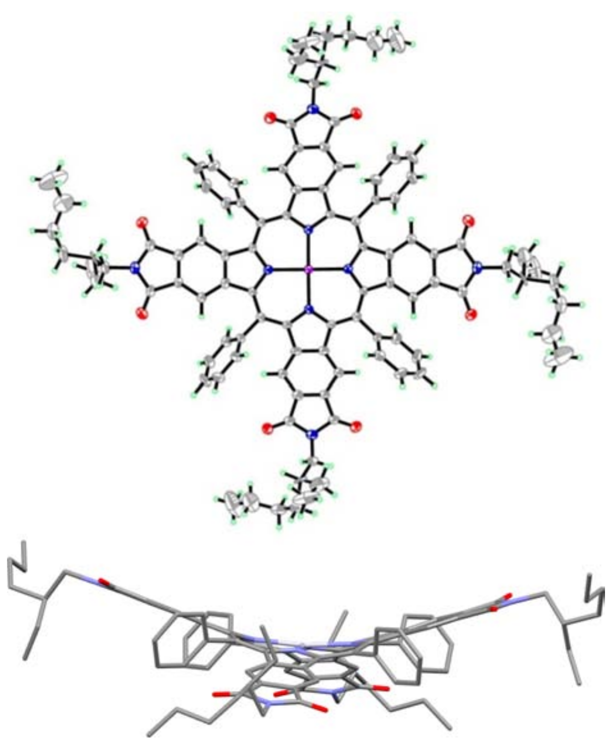

Figure 1. (Top) X-ray structure of (*R*,*S*,*R*,*S*)-**10**. (Bottom) side-view of (*R*,*S*,*R*,*S*)-**10** with hydrogen atoms omitted for clarity.

As is the case for other TBP derivatives, **10** is an exceptionally strong absorber in the blue (λ_{max} = 465 nm, log(ε) = 5.39, Soret band) and red (λ_{max} = 633 nm, log(ε) = 5.20, Q-band) regions of the spectrum (Figure 3). Exciting at either Soret or Q-band leads to near-IR phosphorescence (λ_{max} = 755 nm). The photoluminescence quantum yield (PLQY) of 0.45 was obtained for **10** using PtTPTBP as a reference standard (PLQY = 0.35[10]) measured at rt in argon-degassed toluene. Interestingly, the triplet lifetime of **10** (14 ± 0.1 μs) in an argon-saturated solution is considerably shorter, to our knowledge, than any known platinum porphyrin including the parent PtTPTBP[10] (29.9 μs). This corresponds to an ~3 times faster radiation transition in the former ($k_r = 3.2 \times 10^4\ s^{-1}$ and $1.2 \times 10^4\ s^{-1}$ for **10** and PtTPTBP, respectively), which minimizes quenching and photodegradation processes.

Photodegradation[22] of organic/organometallic dyes is the major drawback to their application, particularly in harvesting solar energy. We hypothesized that the fused electron-withdrawing imide substituents at the periphery of the TPTBP macrocycle would suppress the photooxidation by lowering the HOMO level of the molecule. Indeed, no degradation was observed under ambient light

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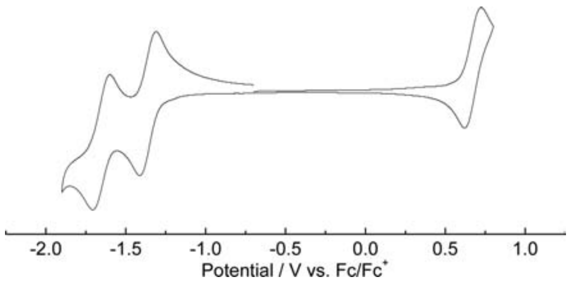

Figure 2. Cyclic voltammetry of **10** in 0.2 M Bu_4NPF_6/CH_2Cl_2 (on Pt disk electrode, scan rate 0.1 V/s).

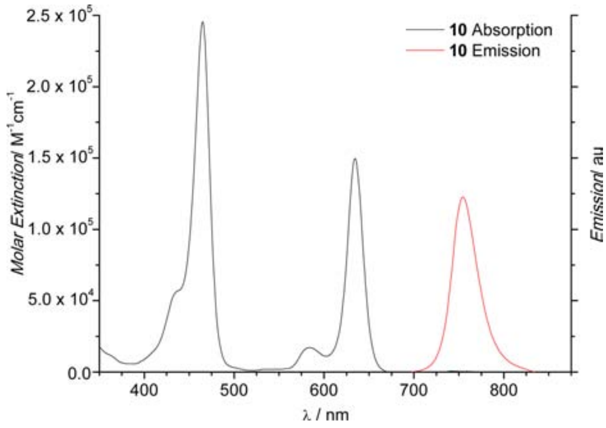

Figure 3. Absorption and emission spectra for **10** in CH_2Cl_2.

for over 8 months, in either the solid state or in toluene solution.

To assess the limits of photostability for **10**, an accelerated photodegradation study (Figure 4) was carried out by illuminating its toluene solution with a 500 W halogen/tungsten lamp at ~90 °C (radiative heating). Almost[23] no degradation was observed when **10** was subjected to these conditions under a nitrogen atmosphere. Even in an air-saturated solution $< 30\%$ degradation was observed after 6 days of continuous irradiation. The parent PtTPTBP showed an ~5 times faster degradation profile under identical conditions, while other common porphyrin dyes, PtOEP and zinc tetraphenylporphyrin (ZnTPP), showed ~20 and ~80 times faster degradation, respectively. The mechanism of the observed photooxidation is based on sensitized generation of singlet oxygen, and the observed stability of **10** under these conditions is remarkable. In fact, the above photodegradation experiment with **10** generates > 200 times as much of solvent decomposition products compared to the loading of the dye (benzylic alcohol, benzaldehyde, benzoic acid, and uncharacterized oligomers; see SI).

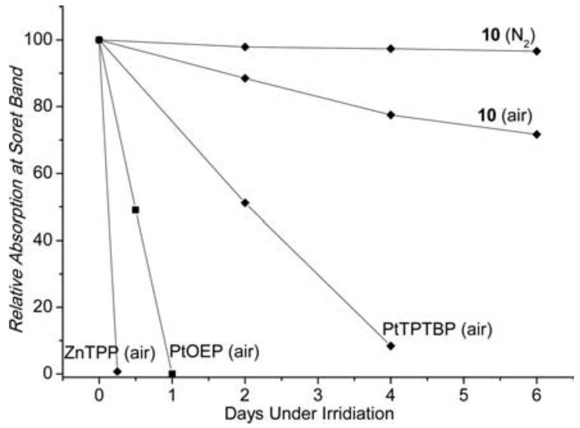

Figure 4. Accelerated photodegradation of porphyrins followed through decrease of Soret band intensity (500 W halogen lamp, 90 °C, PhMe, 10^{-5} M) .

In summary, a large-scale preparation of a new platinum porphyrin dye **10** with fused phthalimide moieties was developed from inexpensive commodity starting materials. **10** was found to be extremely soluble in many organic solvents (up to 600 g/L) and revealed a remarkable photostability that is attributed to a lowered HOMO and shorter luminescence lifetime. A very strong absorption in both the blue and red spectral regions, efficient luminescence at 755 nm ($\Phi_P = 0.45$), and almost no self-absorption make **10** a highly desirable NIR dye for a number of practical applications, including luminescent solar concentrators.

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Supporting Information Available. Experimental procedures and full spectroscopic data for all new compounds; crystallographic data for **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[23] Residual degradation (3%) is likely due to slow penetration of oxygen into the flask over 6 days.

The authors declare no competing financial interest.