

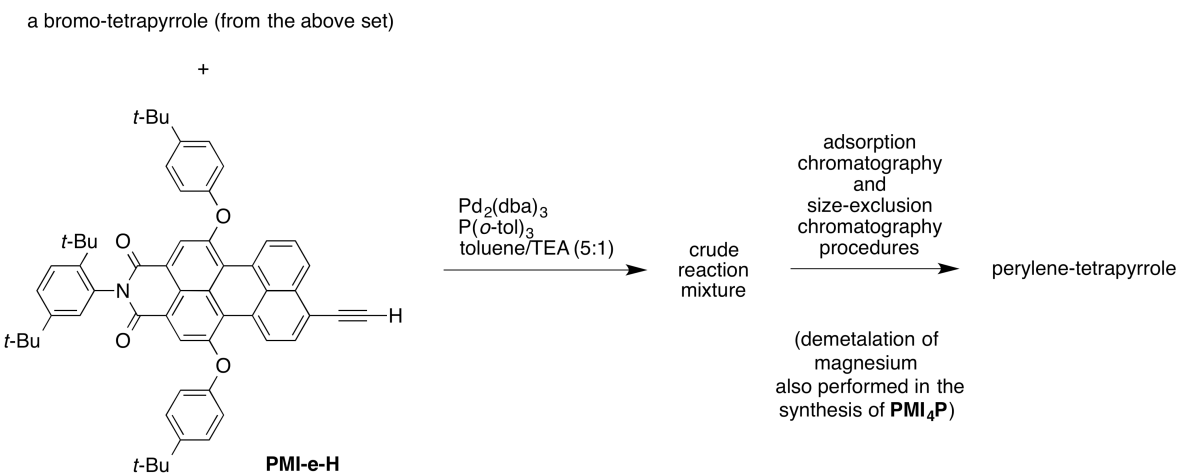
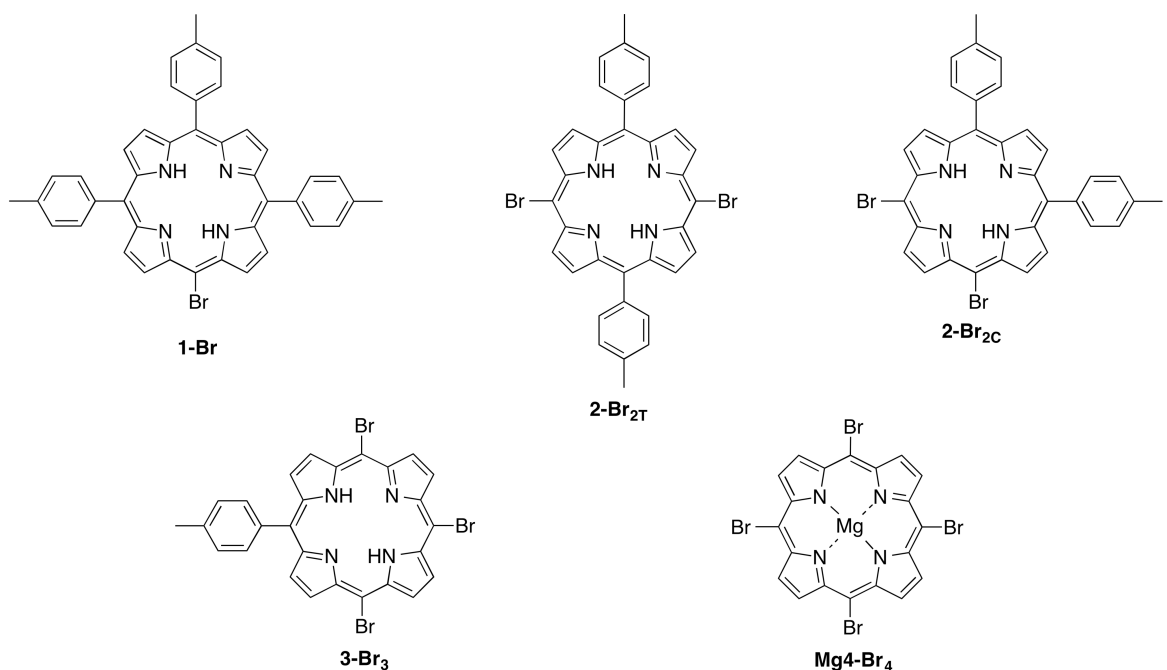
**Supplementary Information (31 pages) for:  
Panchromatic Absorbers for Solar Light-Harvesting**

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<b>Table of Contents</b>	<b>Page</b>
I. Overview of Synthesis	S1–S8
II. General Experimental Methods	S8
III. Source of Literature Compounds	S9
IV. Preparation and Characterization of New Synthetic Compounds	S9–S13
V. Spectroscopic Methods	S13
VI. References	S14–S15
VII. Data	S16–S31
HRMS Data for Porphyrin Building Blocks	S16–S20
MALDI-MS Data of Perylene–Porphyrin Arrays	S21–S26
Analytical SEC (HPLC) Traces of Perylene–Porphyrin Arrays	S27–S31

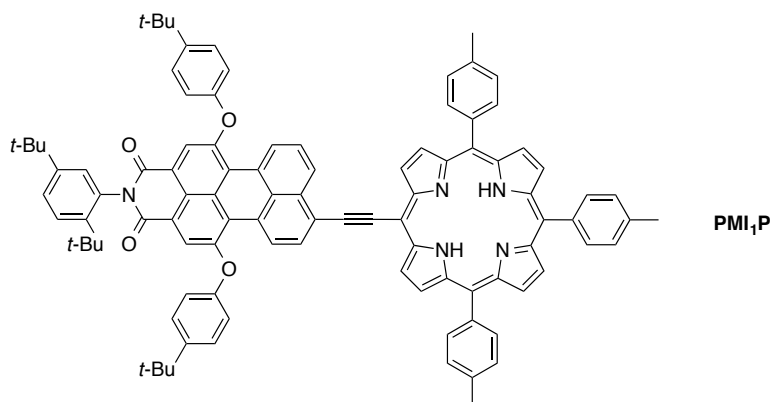
**I. Overview of Synthesis.**

These syntheses follow a modular building block approach wherein a bromo-tetrapyrrole and an ethynyl-erylene (**PMI-e-H**) are linked together in a copper-free,<sup>S1,S2</sup> Sonogashira coupling reaction (Scheme S1). The use of copper-free conditions is essential to avoid adventitious copper insertion into the porphyrin.<sup>S1</sup> Purification is achieved by a combination of column chromatography and preparative size-exclusion chromatography (SEC).<sup>S3,S4</sup> The preparative SEC is carried out in toluene on cross-linked polystyrene columns. Typically, a three-column sequence is employed: (1) a first silica column to remove reactants, catalyst species, and small-molecule byproducts; (2) a preparative SEC column to separate the target array from array intermediates and/or high molecular weight material (HMWM, often oligomeric in nature); and (3) a second silica column to remove any substances (e.g., polystyrene-derived compounds) that have bled from the SEC column.<sup>S3,S4</sup> Due to the relative size of the perylene–monoimide moiety, the presence of an additional perylene unit gives rise to arrays that can be separated by SEC, even if inseparable via adsorption chromatography. Ease of separation diminishes as additional perylene units are attached and a broad range of undesired species are present in the crude reaction mixture. The homogeneity of the arrays is assessed by analytical SEC on an HPLC instrument.<sup>S3,S4</sup>



**Scheme S1.** Modular synthesis of perylene–tetrapyrrole arrays.

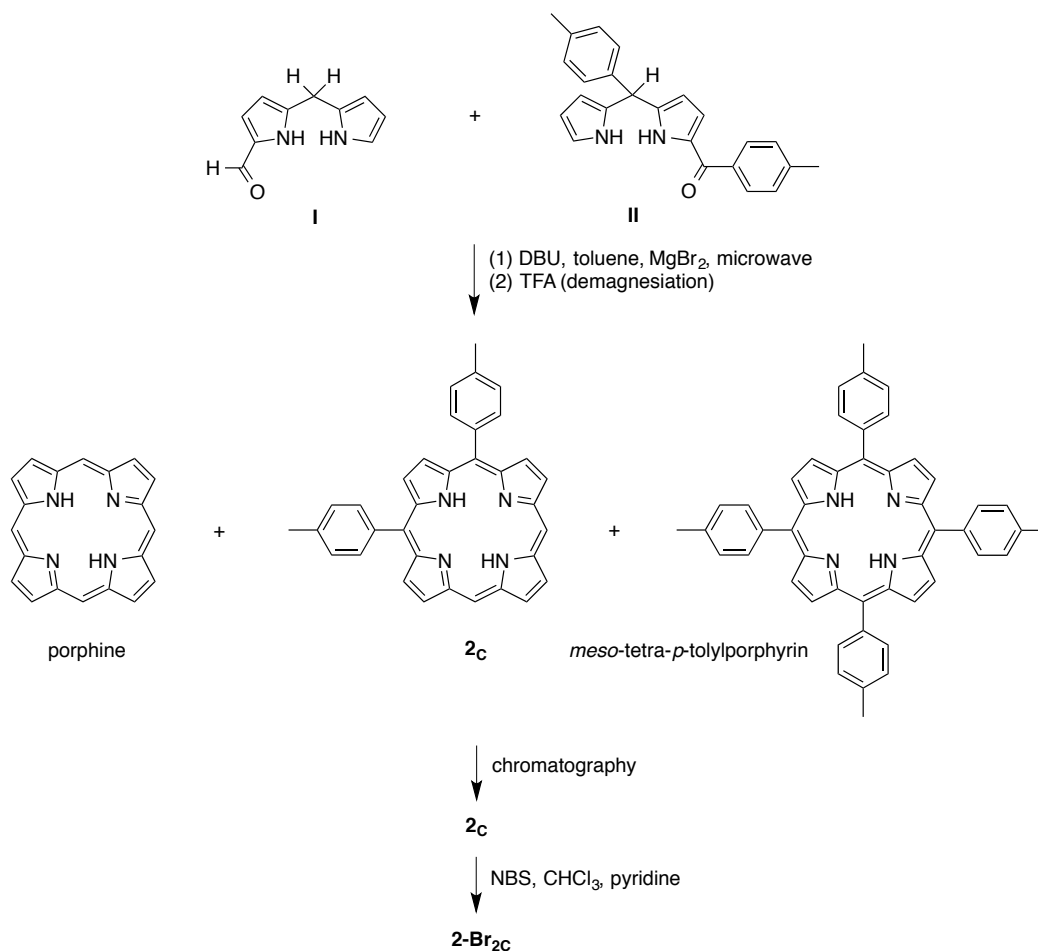
**PMI<sub>1</sub>P.** The synthesis of the porphyrin building block **1-Br** has been reported via the condensation of dipyrromethane and the dicarbinol derived from 1,9-di-*p*-toluoyl-5-*p*-tolylidipyrromethane.<sup>S5-S7</sup> Sonogashira coupling of porphyrin **1-Br** and perylene **PMI-e-H** generated the perylene–porphyrin in 79% yield, the highest among the entire set. The perylene–porphyrin dyad exhibits a green hue in solution (versus dark purple for the remaining four perylene–porphyrin arrays). The dyad **PMI<sub>1</sub>P** was purified with ease using the aforementioned combination of silica gel chromatography and SEC. On SEC, the dyad elutes after the polymeric perylene-containing impurities, and before monomeric perylene and porphyrin impurities with satisfactory resolution of the respective bands. Hence, only one SEC column was required for complete purification. Purity was established by analytical SEC.



**Porphyrin Building Block for the Synthesis of  $\text{PMI}_{2\text{C}}\text{P}$ .** A synthesis of *cis*-di-*p*-tolylporphyrin was previously reported by Senge and coworkers<sup>S8</sup> via condensation of tripyrrane, pyrrole and *p*-tolualdehyde. Their reported procedure also formed a small amount of 5-*p*-tolylporphyrin (**3**). We turned to a statistical condensation of a 1-formyldipyrromethane and a corresponding di-substituted 1-acyldipyrromethane employing microwave irradiation<sup>S9</sup> (Scheme S2). There are three possible porphyrins formed in this reaction: (1) porphine, upon self-condensation of the 1-formyldipyrromethane, (2) a “hybrid” *cis*-porphyrin, upon condensation of the 1-formyldipyrromethane with the 1-acyldipyrromethane, and (3) a tetra-substituted porphyrin, upon self-condensation of the 1-acyldipyrromethane. The success of the reaction relies on the typically facile separation of three porphyrins with 0, 2, or 4 meso-substituents.

Thus, statistical reaction of 1-formyldipyrromethane (**I**)<sup>S10</sup> and 1-*p*-toluoyl-5-*p*-tolylidipyrromethane (**II**)<sup>S11</sup> afforded a crude mixture of porphyrins. Analysis of the crude reaction mixture by UV-Vis showed three distinct porphyrin Soret bands corresponding to the three magnesium porphyrins with increasing intensity in the order of Mg(II)-*meso*-tetra-*p*-tolylporphyrin < Mg(II)-porphine < **Mg2<sub>C</sub>**. Magnesium porphyrins are readily demetalated with mild acids.<sup>S12</sup> Addition of trifluoroacetic acid (TFA) caused demagnesiation (i.e., demetalation of the chelated magnesium). The resulting mixture of free-base porphyrins was subjected to adsorption (silica) column chromatography. The separation is facilitated by the terribly poor solubility of porphine. The *meso*-tetra-*p*-tolylporphyrin, however, streaked into the **2<sub>C</sub>** band resulting in the isolation of **2<sub>C</sub>** with a 2% impurity (based on  $\beta$ -pyrrole proton integration) of *meso*-tetra-*p*-tolylporphyrin. Given that the latter can undergo neither *meso*-bromination nor reaction with the ethynyl-perylene, the impurity was carried through, to be removed by SEC following coupling with **PMI-e-H**.

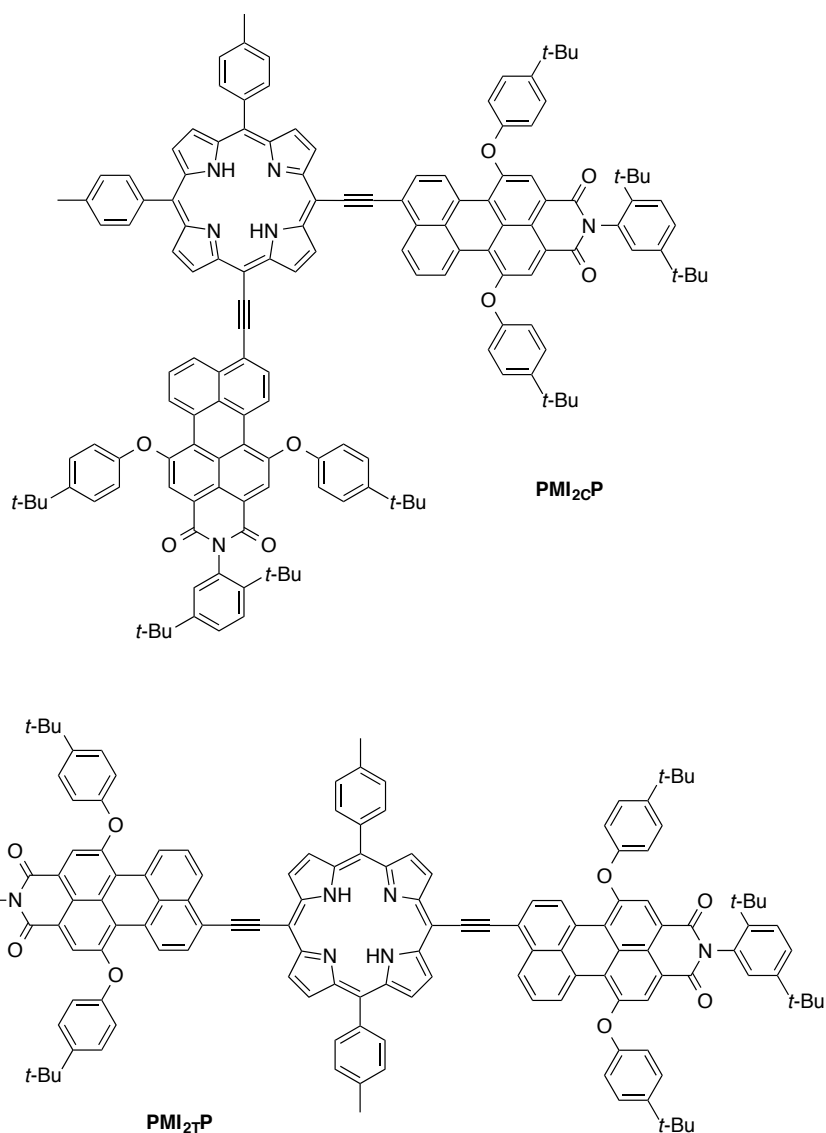
A synthesis of the dibromo-porphyrin building block **2-Br<sub>2T</sub>** was previously reported<sup>S13</sup> via the acid-catalyzed condensation of dipyrromethane and *p*-tolualdehyde followed by dibromination (a procedure first reported by Therien and coworkers<sup>S14</sup>). The conditions employed for the *trans*-dibromination were used analogously for the bromination of **2<sub>C</sub>**, although a 15% decrease in yield was observed in the *cis* case.



**Scheme S2.** Synthesis of 5,10-dibromo-15,20-di-*p*-tolylporphyrin (**2-Br<sub>2</sub>C**).

**PMI<sub>2C</sub>P** and **PMI<sub>2T</sub>P**. In the case of **PMI<sub>2T</sub>P**, a sizeable amount of a dyad (i.e., a porphyrin bearing a single perylene) was observed during SEC purification (eluted as a green band). To suppress formation of the dyad in the coupling reaction leading to **PMI<sub>2C</sub>P**, 2.4 equivalents of ethynyl-*p*-erylene were employed (compared to 2 equivalents in the *trans* case), which resulted in a noticeable decline in the corresponding dyad upon SEC analysis. Although the dyad species was never completely purified in either the *trans* or the *cis* case, the rough absorption spectra matched that of **PMI<sub>1</sub>P**.

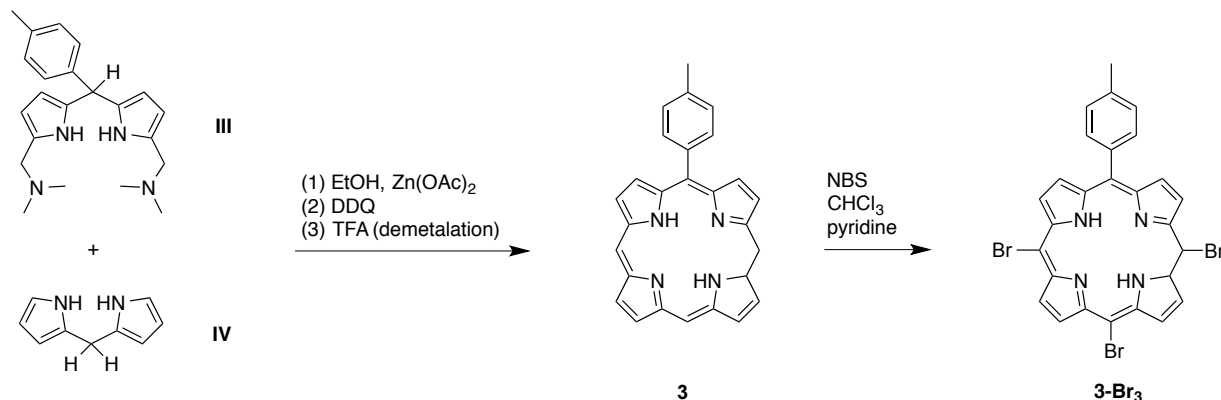
In addition to the undesired dyad, a small amount of higher molecular weight material (HMWM) eluted slightly before the target triad (**PMI<sub>2C</sub>P** or **PMI<sub>2T</sub>P**) in SEC. This HMWM was readily separable in the *trans* case; however, separation proved to be a more arduous task in the *cis* case. The latter HMWM was slightly less polar, eluting before but streaking into the band of the target **PMI<sub>2C</sub>P**. To facilitate column separation, the mixture was metalated with zinc, thereby causing an increase in polarity of the porphyrin-containing compounds and hence affording a more pronounced separation from the HMWM. After purification by silica chromatography, the zinc-containing analogue of **PMI<sub>2C</sub>P** was demetalated to regenerate the free base porphyrin; however, the metalation and demetalation procedure resulted in ~60% loss of material due to significant retention during chromatography. For both arrays, purity was established by analytical SEC.



**Porphyrin Building Block for the Synthesis of PMI<sub>3</sub>P.** A synthesis of the zinc chelate of 5-*p*-tolylporphyrin (**3**) via a metal-mediated condensation of 1,9-bis-(*N,N*-dimethylaminomethyl)-5-*p*-tolylodipyrromethane (**III**)<sup>S15</sup> and dipyrromethane (**IV**)<sup>S16</sup> was previously reported;<sup>S15</sup> however, only a spectroscopic yield was determined (19%) and no isolation was attempted. Using the reported procedure, we obtained the zinc chelate (**Zn3**) in 11% (isolated) yield (Scheme S3).

The bromination conditions employed are analogous to those for *meso*-dibromination; however, somewhat more forcing conditions were required to bring the reaction to completion. A total reaction time of 4.5 h (versus 30 min for dibromination) and 1.9 equivalents of NBS per *meso* site (compared to 1.1) were required. The reaction was maintained at 0 °C for the entire duration in order to suppress undesired bromination of the β-positions. Analysis of the crude reaction mixture, after the 4.5 h, by <sup>1</sup>H NMR spectroscopy gave a tribromo : dibromo : monobromo ratio of 88.9 : 9.0 : 2.1 (based on *p*-tolyl methyl peak integration), with the identity of each species in the mixture confirmed by MALDI-MS. After workup and purification, <sup>1</sup>H

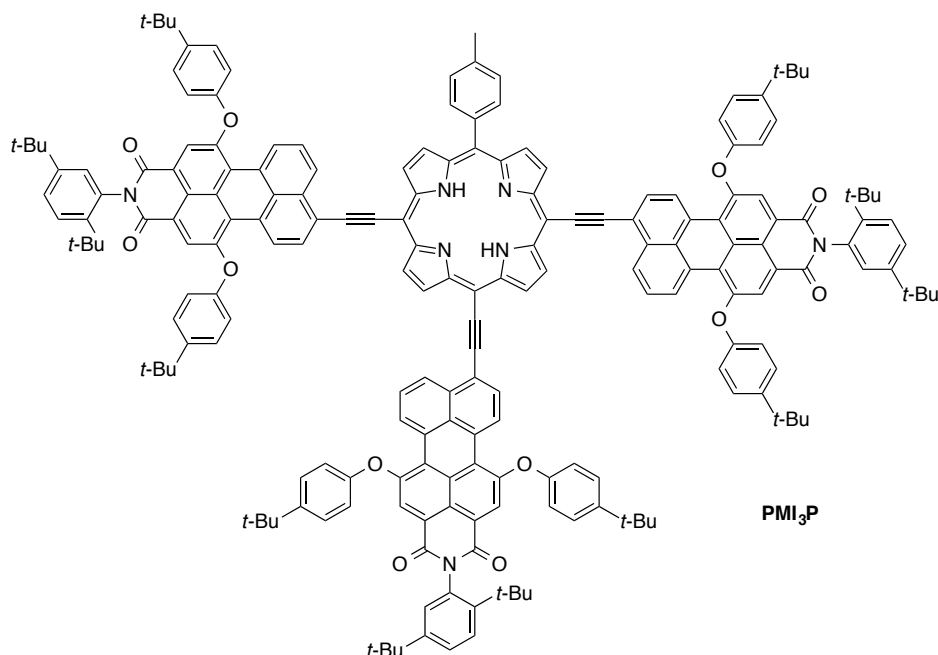
NMR spectroscopy of the isolated **3-Br<sub>3</sub>** showed only one *p*-tolyl methyl singlet; on the other hand, MALDI-MS showed trace amounts of undesired brominated species. A very small peak in MALDI-MS corresponding to a tetrabrominated species was also observed, most likely due to small amounts of β-bromination of the tribromo-porphyrin. The estimated purity of **3-Br<sub>3</sub>** was >98%.



**Scheme S3.** Synthesis of 5,10,15-tribromo-20-*p*-tolylporphyrin (**3-Br<sub>3</sub>**).

**PMI<sub>3</sub>P.** In the coupling reaction to form **PMI<sub>3</sub>P**, slightly more equivalents of ethynyl-*p*erylene (1.3 per bromo) were used compared to that for *p*erylene-porphyrin arrays containing one or two *p*erylenes. Upon analysis of the crude reaction mixture by MALDI-MS, the mono-, bis- and tris-substituted species were observed. Assuming comparable ionization efficiencies, the mono- and bis-species were present in roughly the same quantity, and significantly diminished compared to the tris-*p*erylene species. Purification by SEC gave no clear resolution between the target tetrad **PMI<sub>3</sub>P** and a triad species. As such, the eluting components were fractionated many times, and the purity of each fraction was accessed using MALDI-MS. An absorption spectrum of the co-eluting species resembled that of the *cis*-(**PMI**)<sub>2</sub>**P**. The target tetrad **PMI<sub>3</sub>P** was obtained in pure form as established by analytical SEC.

All attempts to obtain a <sup>1</sup>H NMR spectrum of **PMI<sub>3</sub>P** were to no avail, despite use of CDCl<sub>3</sub>, toluene-*d*<sub>8</sub>, THF-*d*<sub>6</sub>, and CS<sub>2</sub> (shimmed with C<sub>6</sub>D<sub>6</sub>). The solvent CS<sub>2</sub> is known to be effective for solubilization of large aromatic compounds.<sup>S17,S18</sup> For *p*erylene-porphyrin arrays containing ≤2 *p*erylene units, the aromatic region in the <sup>1</sup>H NMR spectrum was resolvable in dilute solution. However, the introduction of additional units resulted in very broad, nondescript, irresolvable peaks, even at low concentrations. The provisional structural assignment of **PMI<sub>3</sub>P** consequently rests heavily on the mass spectrum, which shows the expected composition, and analytical SEC, which shows the elution prior to that for **PMI<sub>2</sub>C****P** and **PMI<sub>2</sub>T****P**. While not proof of structure, the spectral changes along the series **PMI<sub>1</sub>P**, **PMI<sub>2</sub>T****P**, **PMI<sub>2</sub>C****P**, and **PMI<sub>3</sub>P** form a coherent progression, which, taken together with the mass data and analytical SEC data, are self-consistent in supporting the proposed structure.

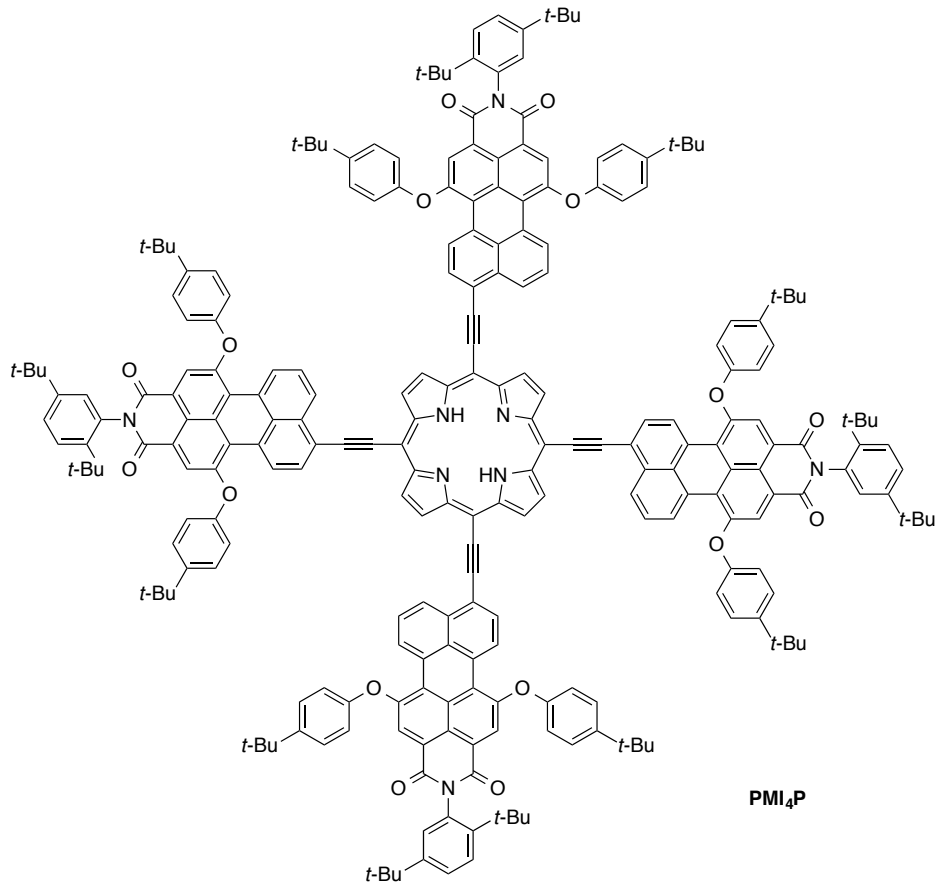


**PMI<sub>4</sub>P.** Porphine is hideously insoluble, yet the solubility is profoundly increased for the corresponding magnesium chelate. Indeed, the tetrabromo derivative of magnesium porphine (**Mg4-Br<sub>4</sub>**) has been reported by bromination of magnesium porphine with 4.7 equivalents of *N*-bromoacetamide at 0 °C.<sup>S19</sup> We prepared magnesium porphine (**Mg4**) by the self-condensation of 1-formyldipyrromethane (**I**) following a reported method.<sup>S20</sup> The tetrabromo derivative **Mg4-Br<sub>4</sub>** was prepared as described,<sup>S19</sup> and employed directly for coupling with **PMI-e-H**. Upon coupling, the presence of the *tert*-butylaryl-substituted perylene groups afforded solubility of the resulting arrays. Because the magnesium chelated tetrabromo-porphyrin was employed, a demetalation step was required after the coupling reaction. As stated above, magnesium porphyrins are acid labile, and can be typically removed under mild acidic conditions; for example, silica gel is sufficiently acidic to displace the magnesium.<sup>S12</sup>

The crude reaction mixture, which contained a set of magnesium porphyrin-(perylene)<sub>n</sub> arrays (n = 1–4) due to incomplete coupling, was dissolved in toluene and placed in a separatory funnel. Washing the toluene solution twice with 1 M HCl resulted in no demetalation of the pentad (n = 4); however, MALDI-MS showed the presence of demetalated perylene-porphyrin dyad species (n = 1). To ensure complete demetalation, the toluene mixture was treated TFA, thereby forming the free base pentad **PMI<sub>4</sub>P**.

The purification of **PMI<sub>4</sub>P** was carried out as follows. First, a silica column removed unreacted ethynylperylene (**PMI-e-H**) and catalyst species. Second, an SEC column afforded a small amount of pure **PMI<sub>4</sub>P**, as well as impure fractions containing **PMI<sub>4</sub>P** [the main impurity co-eluting with the pentad (n = 4) on the SEC column was the tetrad (n = 3) as observed by absorption spectroscopy]. The few mg of pure **PMI<sub>4</sub>P** obtained in this manner by a single SEC column sufficed for characterization and photophysical studies. The impure fractions were subjected to subsequent purification to obtain additional pure **PMI<sub>4</sub>P**. However, not all of the impure fractions were completely purified. Regardless, it warrants emphasis that a total 14 mg of pure **PMI<sub>4</sub>P** was obtained. Purity was established by analytical SEC. As with **PMI<sub>3</sub>P**, a quality <sup>1</sup>H NMR spectrum could not be obtained for **PMI<sub>4</sub>P**. The provisional structural

assignment of **PMI<sub>4</sub>P** consequently rests heavily on the mass spectrum, which shows the expected composition, and analytical SEC, which shows the elution prior to that for **PMI<sub>3</sub>P**. While not proof of structure, the spectral changes along the series **PMI<sub>1</sub>P**, **PMI<sub>2T</sub>P**, **PMI<sub>2C</sub>P**, (**PMI<sub>3</sub>P**) and **PMI<sub>4</sub>P** form a coherent progression, which, taken together with the mass data and analytical SEC data, are self-consistent in supporting the proposed structure.



## II. General Experimental Methods.

The arrays were prepared as described for prior perylene–porphyrin dyads<sup>13</sup> using established copper-free Pd-mediated coupling reactions under argon.<sup>S1,S2</sup> Preparative size-exclusion chromatography (SEC) was performed using BioRad Bio-Beads SX-1 (200–400 mesh) beads as described in detail previously for multiporphyrin arrays.<sup>S3,S4</sup> Analytical SEC was performed using three columns in series, as described previously.<sup>S3,S4</sup> The three-column arrangement was composed of 50 Å (300 x 7.5 mm), 100 Å (300 x 7.5 mm), and 500 Å (300 x 7.5 mm) columns in sequence (typical  $t_M \sim 24\text{--}29$  min). Toluene (HPLC grade) was the eluting solvent with a flowrate of 0.8 mL/min. A photodiode detector enabled multi-wavelength absorption detection, also as described in detail previously for multiporphyrin arrays. All commercially available materials were used as received. <sup>1</sup>H NMR (300 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded in CDCl<sub>3</sub> at room temperature unless noted otherwise. Mass spectra were obtained by laser desorption mass spectrometry (MALDI-MS) in the presence of a matrix [POPOP, 1,4-bis(5-phenyloxazol-2-yl)benzene] unless noted otherwise.<sup>S21-S23</sup> Absorption spectral data reported below were collected in toluene at room temperature.



### III. Source of Literature Compounds.

Two photophysical reference compounds include 5,10,15-triphenyl-20-(2-phenylethynyl)porphyrin (**P**)<sup>S5,S24</sup> and 9-[2-(trimethylsilyl)ethynyl]-1,6-bis(4-*tert*-butylphenoxy)-*N*-(2,5-di-*tert*-butylphenyl)-3,4-perylenedicarboximide (**PMI**).<sup>S25-S27</sup>

The following synthetic precursors to the perylene-porphyrin arrays were prepared as described in the literature: 1-formyldipyrrromethane (**I**),<sup>S10</sup> 1-*p*-toluoyl-5-*p*-tolyldipyrrromethane (**II**),<sup>S11</sup> 1,9-bis(*N,N*-dimethylaminomethyl)-5-*p*-tolyldipyrrromethane (**III**),<sup>S15</sup> dipyrromethane (**IV**),<sup>S16</sup> 5-bromo-10,15,20-tri-*p*-tolylbromoporphyrin (**1-Br**),<sup>S5</sup> 5,15-dibromo-10,20-di-*p*-tolylporphyrin (**2-Br<sub>2T</sub>**),<sup>S13</sup> Mg(II)-5,10,15,20-tetrabromoporphyrin (**Mg4-Br<sub>4</sub>**),<sup>S19</sup> and 9-ethynyl-1,6-bis(4-*tert*-butylphenoxy)-*N*-(2,5-di-*tert*-butylphenyl)-3,4-perylenedicarboximide (**PMI-e-H**).<sup>S25-S27</sup>

### IV. Preparation and Characterization of New Synthetic Compounds.

#### A. Synthesis of Porphyrins.

**5,10-Di-*p*-tolyldiporphyrin (2c).** Following a procedure for the synthesis of *cis*-substituted porphyrins,<sup>S9</sup> a 10 mL glass vial was treated with samples of 1-formyldipyrrromethane (**I**, 40.0 mg, 0.23 mmol), 1-*p*-toluoyl-5-*p*-tolyldipyrrromethane (**II**, 81.4 mg, 0.23 mmol), toluene (4.6 mL), and DBU (0.684 mL, 4.56 mmol), and then stirred for 5 min at room temperature. MgBr<sub>2</sub> (252 mg, 1.364 mmol) was then added, the vial was sealed with a cap, and the mixture was placed in a microwave reactor and irradiated at 115 °C for 35 min. Irradiation occurred with a power set point of 100 W, and the pressure typically fluctuated between 30–50 psi. The reaction process was repeated until a total of 350 mg (2.01 mmol) of **I** and 711.9 mg (2.01 mmol) of **II** had been consumed. The crude mixtures of each run were combined, washed (water, brine), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated. The resulting crude mixture was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (40 mL), treated with TFA (0.7 mL) and stirred for 1.5 h. The reaction was quenched by addition of TEA (1.0 mL). The organic layer was washed (water, brine), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated. The crude product was purified via column chromatography [silica, hexanes/ethyl acetate (9:1)] to yield a purple solid (43.5 mg, 4.4%) with a 2% impurity of 5,10,15,20-tetra-*p*-tolyldiporphyrin (based on  $\beta$ -pyrrole proton integration): <sup>1</sup>H NMR  $\delta$  -3.37 (s, 2H), 2.71 (s, 6H), 7.56 (d,  $J$  = 7.70 Hz, 4H), 8.10 (d,  $J$  = 8.06 Hz, 4H), 8.99 (s, 2H), 9.04 (d,  $J$  = 4.40 Hz, 2H), 9.31 (d,  $J$  = 4.77 Hz, 2H), 9.40 (s, 2H), 10.18 (s, 2H); <sup>13</sup>C NMR  $\delta$  21.75, 29.94, 104.22, 127.63, 131.10-132.10 (m), 134.799, 137.589, 139.409; HRMS (ESI) found  $m/z$  491.22303, calcd for C<sub>34</sub>H<sub>27</sub>N<sub>4</sub> [M + H]<sup>+</sup> 491.22302.

**Zn(II)-5-*p*-tolyldiporphyrin (Zn3).** Following a procedure for preparing mono-substituted porphyrins,<sup>S15</sup> samples of 1,9-bis(*N,N*-dimethylaminomethyl)-5-*p*-tolyldipyrrromethane (**III**, 350.0 mg, 1 mmol) and dipyrromethane (**IV**, 146.1 mg, 1 mmol) were dissolved in EtOH (100 mL) and treated with Zn(OAc)<sub>2</sub> (1.834 g, 10 mmol). The resulting mixture was heated at reflux for 2 h, and then allowed to cool to room temperature. DDQ (680 mg, 3 mmol) was then added, upon which the reaction mixture instantly darkened. The mixture was stirred for 15 min, treated with TEA (0.710 mL) and concentrated. The crude product was purified via column chromatography [silica, hexanes/CH<sub>2</sub>Cl<sub>2</sub> (2:1) to (3:2)], and fractions containing the desired compound were concentrated to a solid. The solid was treated with HPLC-grade hexanes, sonicated, centrifuged and the supernatant removed to yield a red solid (50.2 mg, 11%): <sup>1</sup>H NMR  $\delta$  2.76 (s, 3H), 7.61 (d,  $J$  = 7.43 Hz, 2H), 8.17 (d,  $J$  = 7.98 Hz, 2H), 9.20 (d,  $J$  = 4.40 Hz, 2H),

9.46 (d,  $J = 4.40$  Hz, 2H), 9.52 (m, 4H), 10.26 (s, 1H), 10.32 (s, 2H); HRMS (ESI) found  $m/z$  463.08817, calcd for  $C_{27}H_{19}N_4Zn [M + H]^+$  463.09009. Limited solubility precluded obtaining a  $^{13}C$  NMR spectrum.

**5-*p*-Tolylporphyrin (3).** A sample of **Zn3** (40.0 mg, 0.087 mmol) was dissolved in  $CH_2Cl_2$  (20 mL) and treated with TFA (331  $\mu$ L). The resulting mixture was stirred for 1 h, upon which TLC analysis showed a lingering presence of **Zn3**. The mixture was treated with additional TFA (250  $\mu$ L) and stirred for another 1 h. The organic layer was washed with sodium bicarbonate (2x), dried ( $Na_2SO_4$ ), and concentrated. The crude product was purified via column chromatography [silica, hexanes/ $CH_2Cl_2$  (1:1)] to give a brownish purple solid (30.0 mg, 86%):  $^1H$  NMR  $\delta$  -3.59 (s, 2H), 2.74 (s, 3H), 7.61 (d,  $J = 7.64$  Hz, 2H), 8.16 (d,  $J = 7.94$  Hz, 2H), 9.13 (d,  $J = 4.58$  Hz, 2H), 9.42 (d,  $J = 4.58$  Hz, 2H), 9.50 (q,  $J = 4.58$  Hz, 3.36 Hz, 4H), 10.27 (s, 1H), 10.34 (s, 2H); HRMS (ESI) found  $m/z$  401.17626, calcd for  $C_{27}H_{21}N_4 [M + H]^+$  401.17607. Limited solubility precluded obtaining a  $^{13}C$  NMR spectrum.

## B. Bromination of Porphyrins.

**5,10-Dibromo-15-20-di-*p*-tolylporphyrin (2-Br<sub>2C</sub>).** A sample of **2<sub>C</sub>** (37.0 mg, 0.075 mmol), with a small amount of *meso*-tetra-*p*-tolylporphyrin impurity, was dissolved in  $CHCl_3$  (18.75 mL) and chilled to 0 °C. The solution was treated with NBS (29.5 mg, 0.166 mmol) and pyridine (75  $\mu$ L), and subsequently stirred for 30 min maintained at 0 °C. The crude reaction mixture was concentrated and purified via column chromatography [silica, hexanes/ $CH_2Cl_2$  (2:1)]. The solid obtained was treated with HPLC-grade hexanes, sonicated, centrifuged and the supernatant removed to yield a purple solid (40.8 mg, 84%):  $^1H$  NMR  $\delta$  -2.953 (br, s, 2H), 2.70 (s, 6H), 7.54 (d,  $J = 8.29$  Hz, 4H), 8.01 (d,  $J = 7.80$  Hz, 4H), 8.75 (s, 2H), 8.82 (d,  $J = 4.88$  Hz, 2H), 9.52 (d,  $J = 4.40$  Hz, 2H), 9.52 (s, 2H)\*;  $^{13}C$  NMR  $\delta$  21.75, 103.33, 121.93, 127.76, 132.43 (m), 134.62, 137.93, 138.77; HRMS (ESI) found  $m/z$  647.04360, calcd for  $C_{34}H_{25}N_4Br_2 [M + H]^+$  647.04405. \*The typically separate singlet and doublet coincided to form a skewed doublet.

**5,10,15-Tribromo-20-*p*-tolylporphyrin (3-Br<sub>3</sub>).** A sample of **3** (30 mg, 0.075 mmol) was dissolved in  $CHCl_3$  (18.75 mL) and chilled to 0 °C. The solution was then treated with NBS (43.3 mg, 0.247 mmol) and pyridine (112.5  $\mu$ L), and subsequently stirred for 1 h maintained at 0 °C. TLC analysis showed a mixture of four distinct species, so additional NBS (15 mg, 0.086 mmol) was added, and the reaction continued for another 2 h. A mixture was still observed, so additional NBS (15 mg, 0.086 mmol) was added, and the reaction continued for 1 h. The crude product was purified via column chromatography [silica, hexanes/ $CH_2Cl_2$  (2:1) to (1:2)]. The solid obtained was treated with HPLC-grade hexanes, sonicated, centrifuged, and the supernatant removed to yield a purple solid (36.0 mg, 76%):  $^1H$  NMR  $\delta$  -3.10 (br, s, 2H), 2.72 (s, 3H), 7.58 (d,  $J = 7.70$  Hz, 2H), 8.00 (d,  $J = 7.70$  Hz, 2H), 8.80 (m, 2H), 9.51 (m 6H); HRMS (ESI) found  $m/z$  634.90826, calcd for  $C_{27}H_{18}N_4Br_3 [M + H]^+$  634.90761.

## C. Synthesis of Perylene–Porphyrin Arrays.

**5-[1,6-Bis(4-*tert*-butylphenoxy)-*N*-(2,5-di-*tert*-butylphenyl)-3,4-(perylene-1,6-dicarboximide-9-yl)ethynyl]-10,15,20-di-*p*-tolylporphyrin (PMI<sub>1</sub>P).** A solution of toluene/TEA (5:1) was degassed by bubbling argon for 30 min in a round-bottom flask. A Schlenk flask containing samples of **PMI-e-H** (90.73 mg, 109.392  $\mu$ mol) and **1-Br** (60.0 mg, 91.16  $\mu$ mol) was treated with 42 mL of the degassed toluene/TEA solution and subjected to three

freeze-pump-thaw cycles. The resulting mixture was treated with Pd<sub>2</sub>(dba)<sub>3</sub> (12.5 mg, 13.7 μmol) and P(*o*-tol)<sub>3</sub> (33.3 mg, 109.4 μmol), subjected to two additional freeze-pump-thaw cycles, heated to 60 °C and stirred for 3 h. The crude mixture was washed out of the Schlenk flask with CH<sub>2</sub>Cl<sub>2</sub> and concentrated to a dark solid. The crude solid was partially purified via a short silica column [hexanes/CH<sub>2</sub>Cl<sub>2</sub> (3:2) to (1:1)]. Fractions containing the target compound were combined and further purified via SEC (toluene, 0.1 mL/min). A final silica column [neat hexanes to hexanes/CH<sub>2</sub>Cl<sub>2</sub> (1:1)] removed any remaining impurities to yield a dark green solid (100.9 mg, 79%): <sup>1</sup>H NMR δ -2.20 (br, s, 2H), 1.28–1.36 (m, 32H), 2.70 (s, 3H), 2.72 (s, 6H), 6.91 (s, 1H), 6.96 (d, *J* = 1.8 Hz, 1H), 7.13–7.19 (m, 6H), 7.40–7.48 (m, 5H), 7.54–7.61 (m, 8H), 7.91 (t, *J* = 8.53 Hz, 1H), 8.05–8.11 (m, 6H), 8.35–8.38 (m, 3H), 8.78 (s, 4H), 8.98 (d, *J* = 4.95 Hz, 2H), 9.18 (d, *J* = 7.43 Hz, 1H), 9.56 (d, *J* = 8.25, 2H), 9.83 (d, *J* = 4.68 Hz, 2H); λ<sub>abs</sub> (toluene) 431, 532, 614, 688 nm; MALDI-MS found *m/z* 1408.6, calcd for C<sub>99</sub>H<sub>86</sub>N<sub>5</sub>O<sub>4</sub> [M + H]<sup>+</sup> 1408.6681. Homogeneous by analytical SEC (t<sub>M</sub> = 28.9 min).

**5,15-Bis[1,6-bis(4-*tert*-butylphenoxy)-*N*-(2,5-di-*tert*-butylphenyl)-3,4-(perylene-9-yl)ethynyl]-10,20-di-*p*-tolylporphyrin [PMI<sub>2T</sub>P].** A solution of toluene/TEA (5:1) was degassed by bubbling argon for 30 min in a round-bottom flask. A Schlenk flask containing samples of PMI-e-H (101 mg, 120.0 μmol) and 2-Br<sub>2T</sub> (38.8 mg, 60.0 μmol) was treated with 45 mL of the degassed toluene/TEA solution and subjected to three freeze-pump-thaw cycles. The resulting mixture was treated with Pd<sub>2</sub>(dba)<sub>3</sub> (16.5 mg, 18.0 μmol) and P(*o*-tol)<sub>3</sub> (43.8 mg, 144 μmol), subjected to two additional freeze-pump-thaw cycles, heated to 60 °C and stirred for 3 h. The crude mixture was washed out of the Schlenk flask with CH<sub>2</sub>Cl<sub>2</sub> and concentrated to a dark solid. The crude solid was partially purified via a short silica column [hexanes/CH<sub>2</sub>Cl<sub>2</sub> (2:1) to (1:1)]. Fractions containing the target compound were combined and further purified via SEC (toluene, 0.1 mL/min). A final silica column [hexanes/CH<sub>2</sub>Cl<sub>2</sub> (2:1) to (1:1)] removed any remaining impurities to yield a dark green solid (82 mg, 62%): <sup>1</sup>H NMR δ -1.79 (s, br, 2H), 1.28–1.36 (m, 72H), 2.74 (s, 6H), 6.99 (d, *J* = 2.13 Hz, 2H), 7.09–7.13 (m, 8H), 7.41–7.45 (m, 10H), 7.55 (d, *J* = 8.81 Hz, 2H), 7.61 (d, *J* = 7.66 Hz, 4H), 7.82 (t, *J* = 8.05 Hz, 2H), 8.10 (d, *J* = 7.66 Hz, 4H), 8.28 (d, *J* = 8.12 Hz, 2H), 8.31 (s, 2H), 8.32 (s, 2H), 8.90 (d, *J* = 4.64 Hz, 4H), 9.10 (d, *J* = 8.12 Hz, 2H), 9.39–9.45 (m, 4H), 9.75 (d, *J* = 4.64 Hz, 4H); λ<sub>abs</sub> (toluene) 430, 475, 537, 636, 726 nm; MALDI-MS found *m/z* 2145.9, calcd for C<sub>150</sub>H<sub>133</sub>N<sub>6</sub>O<sub>8</sub> [M + H]<sup>+</sup> 2146.0186. Homogeneous by analytical SEC (t<sub>M</sub> = 26.5 min).

**5,10-Bis[1,6-bis(4-*tert*-butylphenoxy)-*N*-(2,5-di-*tert*-butylphenyl)-3,4-(perylene-9-yl)ethynyl]-15,20-di-*p*-tolylporphyrin [PMI<sub>2C</sub>P].** A solution of toluene/TEA (5:1) was degassed by bubbling argon for 30 min in a round-bottom flask. A Schlenk flask containing samples of PMI-e-H (61.6 mg, 74.0 μmol) and 2-Br<sub>2C</sub> (20.0 mg, 31.0 μmol) was treated with 23 mL of the degassed toluene/TEA solution and subjected to three freeze-pump-thaw cycles. The resulting mixture was treated with Pd<sub>2</sub>(dba)<sub>3</sub> (8.52 mg, 9.3 μmol) and P(*o*-tol)<sub>3</sub> (22.65 mg, 74.4 μmol), subjected to two additional freeze-pump-thaw cycles, heated to 60 °C and stirred for 3 h. The crude mixture was washed out of the Schlenk flask with CH<sub>2</sub>Cl<sub>2</sub> and concentrated to a dark solid. The crude solid was partially purified via a short silica column [hexanes/CH<sub>2</sub>Cl<sub>2</sub> (2:1) to (1:1)]. Fractions containing the target compound were combined and further purified via SEC [toluene, 0.1 mL/min]. Purification via a final silica column [neat hexanes to hexanes/CH<sub>2</sub>Cl<sub>2</sub> (1:1)] yielded a dark purple solid. The solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (17 mL) and treated with a suspension of Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (280.9 mg, 1.19 mmol) in MeOH (1.7 mL) and stirred overnight at room temperature in dim lighting. The reaction mixture was washed (NaHCO<sub>3</sub>), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated. Purification via

column chromatography [silica, neat hexanes to hexanes/CH<sub>2</sub>Cl<sub>2</sub> (1:1) to neat CH<sub>2</sub>Cl<sub>2</sub>] yielded crude Zn(II)-5,10-bis[1,6-bis(4-*tert*-butylphenoxy)-*N*-(2,5-di-*tert*-butylphenyl)-3,4-(perylene-9-yl)ethynyl]-15,20-di-*p*-tolylporphyrin [**PMI<sub>2</sub>CZnP**] as a dark purple solid (31 mg, 45%, with impurities). The solid was not completely purified and was used in the subsequent step:  $\lambda_{\text{abs}}$  (toluene) 432, 455, 517, 557, 676 nm; MALDI-MS found  $m/z$  2207.9, calcd for C<sub>150</sub>H<sub>131</sub>N<sub>6</sub>O<sub>8</sub>Zn [M + H]<sup>+</sup> 2207.9321.

A sample of partially purified **PMI<sub>2</sub>CZnP** (8.9 mg, 4.0  $\mu\text{mol}$ ) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and treated with TFA (15  $\mu\text{L}$ ). The resulting mixture was stirred for 1.5 h at room temperature and quenched by addition of saturated NaHCO<sub>3</sub>. The organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated. Purification via a short column [silica, neat hexanes to hexanes/CH<sub>2</sub>Cl<sub>2</sub> (1:1) to neat CH<sub>2</sub>Cl<sub>2</sub>] yielded a dark purple solid (6.5 mg, 76%): <sup>1</sup>H NMR  $\delta$  -2.00 (br, s, 2H), 1.30–1.34 (m, 72H), 2.72 (s, 6H), 7.02 (d,  $J$  = 2.2 Hz, 2H), 7.07 (dd,  $J$  = 1.93 Hz, 7.00 Hz, 8H) 7.40–7.56 (m, 10H), 7.56–7.59 (m, 6H), 7.80 (t,  $J$  = 8.25 Hz, 2H), 8.07 (d,  $J$  = 7.98 Hz, 4H), 8.22 (d,  $J$  = 8.25 Hz, 2H), 8.29 (s, 4H), 8.71 (s, 2H), 8.86 (d,  $J$  = 4.68 Hz, 2H), 9.06 (d,  $J$  = 7.98 Hz, 2H), 9.32 (m, 4H), 9.64 (d,  $J$  = 4.40 Hz, 2H), 9.74 (s, 2H);  $\lambda_{\text{abs}}$  (toluene) 424, 451, 542, 638, 720 (sh) nm; MALDI-MS found  $m/z$  2146.0, calcd for C<sub>150</sub>H<sub>133</sub>N<sub>6</sub>O<sub>8</sub> [M + H]<sup>+</sup> 2146.01861. Homogeneous by analytical SEC ( $t_{\text{M}}$  = 26.9 min).

**5,10,15-Tris[1,6-bis(4-*tert*-butylphenoxy)-*N*-(2,5-di-*tert*-butylphenyl)-3,4-(perylene-9-yl)ethynyl]-20-*p*-tolylporphyrin (**PMI<sub>3</sub>P**).** A solution of toluene/TEA (5:1) was degassed by bubbling argon for 30 min in a round-bottom flask. A Schlenk flask containing samples of **PMI-e-H** (178.6 mg, 215.3  $\mu\text{mol}$ ) and **3-Br<sub>3</sub>** (35.0 mg, 55.2  $\mu\text{mol}$ ) was treated with 60 mL of the degassed toluene/TEA solution and subjected to three freeze-pump-thaw cycles. The resulting mixture was treated with Pd<sub>2</sub>(dba)<sub>3</sub> (22.8 mg, 24.8  $\mu\text{mol}$ ) and P(*o*-tol)<sub>3</sub> (60.5 mg, 0.199 mmol), subjected to two additional freeze-pump-thaw cycles, heated to 60 °C and stirred for 3 h. The crude mixture was washed out of the Schlenk flask with CH<sub>2</sub>Cl<sub>2</sub> and concentrated to a dark solid. The crude solid was partially purified via a short silica column [hexanes/CH<sub>2</sub>Cl<sub>2</sub> (1:1)]. Fractions containing the target compound were combined and further purified via SEC [toluene, 0.1 mL/min]. Due to closely eluting impurities (mostly *cis* di-substituted) two more SEC columns, analogous to the first, were run with each producing a pure sample as well as an impure mixture. Combined pure samples were purified via a final silica column [neat hexanes to hexanes/CH<sub>2</sub>Cl<sub>2</sub> (1:1)] to yield a dark purple solid (96.3 mg, 61%):  $\lambda_{\text{abs}}$  (toluene) 420, 548, 710, 717 nm; MALDI-MS found  $m/z$  2882.5, calcd for C<sub>201</sub>H<sub>179</sub>N<sub>7</sub>O<sub>12</sub> [M] 2882.36117. <sup>1</sup>H NMR spectroscopy at room temperature was attempted in CDCl<sub>3</sub>, toluene-*d*<sub>8</sub>, THF-*d*<sub>6</sub>, and CS<sub>2</sub> (shimmed with C<sub>6</sub>D<sub>6</sub>), but in each case, sufficient resolution was not observed. Homogeneous by analytical SEC ( $t_{\text{M}}$  = 25.5 min).

**5,10,15,20-Tetrakis-[1,6-bis(4-*tert*-butylphenoxy)-*N*-(2,5-di-*tert*-butylphenyl)-3,4-(perylene-9-yl)ethynyl]-porphyrin (**PMI<sub>4</sub>P**).** A solution of toluene/TEA (5:1) was degassed by bubbling argon for 30 min in a round-bottom flask. A Schlenk flask containing samples of **PMI-e-H** (74.1 mg, 89.3  $\mu\text{mol}$ ) and **Mg4-Br<sub>4</sub>** (11.5 mg, 17.9  $\mu\text{mol}$ ) was treated with 25 mL of the degassed toluene/TEA solution and subjected to three freeze-pump-thaw cycles. The resulting mixture was treated with Pd<sub>2</sub>(dba)<sub>3</sub> (9.8 mg, 10.7  $\mu\text{mol}$ ) and P(*o*-tol)<sub>3</sub> (26.1 mg, 85.7  $\mu\text{mol}$ ), subjected to two additional freeze-pump-thaw cycles, heated to 60 °C and stirred for 3.5 h. The crude mixture was washed out of the Schlenk flask with CH<sub>2</sub>Cl<sub>2</sub> and concentrated to a dark solid. The crude solid was dissolved in 15 mL of CH<sub>2</sub>Cl<sub>2</sub>, treated with TFA (70  $\mu\text{L}$ ) to remove the magnesium, and stirred at room temperature for 1 h. The resulting mixture was concentrated and partially purified via a short silica column [hexanes/CH<sub>2</sub>Cl<sub>2</sub> (2:1) to neat

CH<sub>2</sub>Cl<sub>2</sub>]. Fractions containing the target compound were combined and further purified via SEC [toluene, 0.1 mL/min]. A pure sample and an impure mixture were obtained from the column; the impure mixture was not pursued. The pure sample was purified via a final silica column, analogous to the first, yielding a dark purple solid (14.2 mg, 22%):  $\lambda_{\text{abs}}$  (toluene) 420, 564, 597, 763 nm; MALDI-MS found  $m/z$  3620.7, calcd for C<sub>252</sub>H<sub>227</sub>N<sub>8</sub>O<sub>16</sub> [M + H]<sup>+</sup> 3620.7196. <sup>1</sup>H NMR spectroscopy at room temperature was attempted in CDCl<sub>3</sub>, but no resolution of peaks was observed. Homogeneous by analytical SEC ( $t_M$  = 24.6 min).

## V. Spectroscopic Methods.

Static absorption (Shimadzu UV-1800) and fluorescence (Horiba Nanolog) measurements were performed at room temperature, as were all other studies. Measurement of the fluorescence quantum yield ( $\Phi_f$ ) and singlet excited-state lifetimes ( $\tau_s$ ) utilized dilute ( $\mu\text{M}$ ) Ar-purged toluene solutions. Samples for  $\Phi_f$  measurements have an absorbance of  $\sim 0.1$  at the excitation wavelength. Static emission measurements employed 2–4 nm excitation and detection bandwidths. Emission spectra were corrected for detection-system spectral response. Fluorescence quantum yields were determined by use of an integrating sphere where the ratio of excitation and emission bands were compared for a blank and a sample to calculate the absolute fluorescence quantum yield (Quanta-Phi, Horiba). Fluorescence lifetimes were obtained utilizing transient absorption decay measurements in which difference spectra (500–750 nm) were measured in 100-ps bins as a function of time (to  $\sim 100$  ns) after a 130 fs excitation flash in the blue-green spectral region (EOS, Ultrafast Systems).

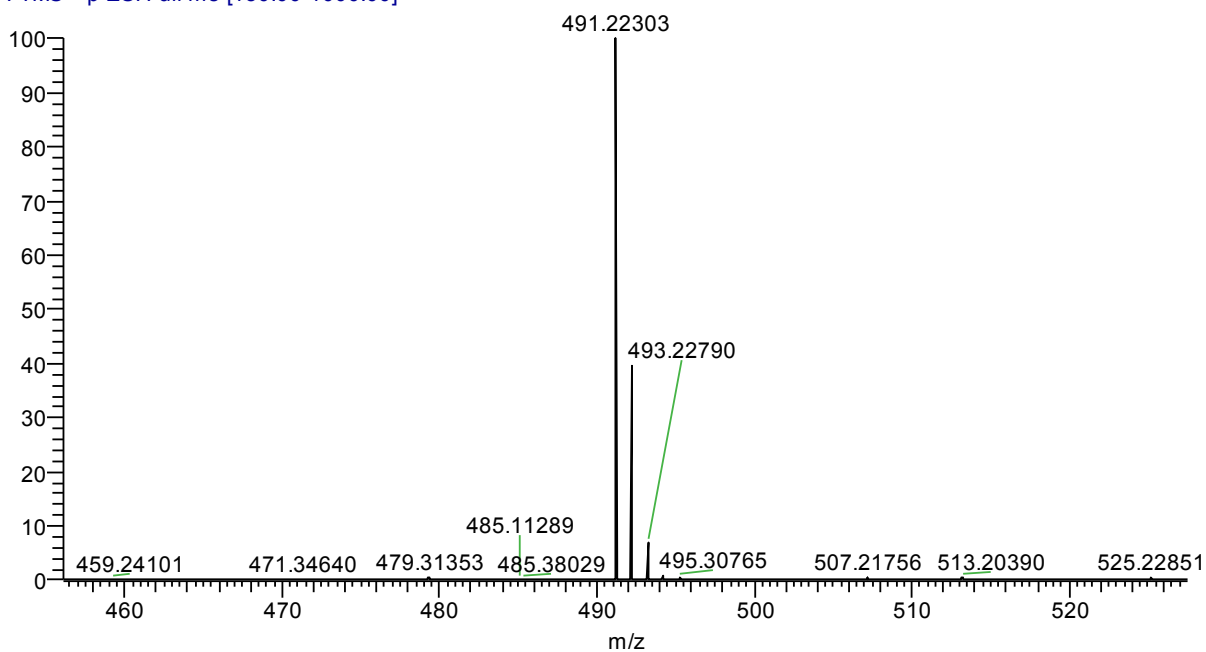
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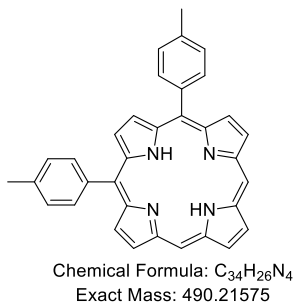
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## VII. Data.

130666 #38-47 RT: 0.22-0.27 AV: 10 NL 3  
T: FTMS + p ESI Full ms [150.00-1000.00]

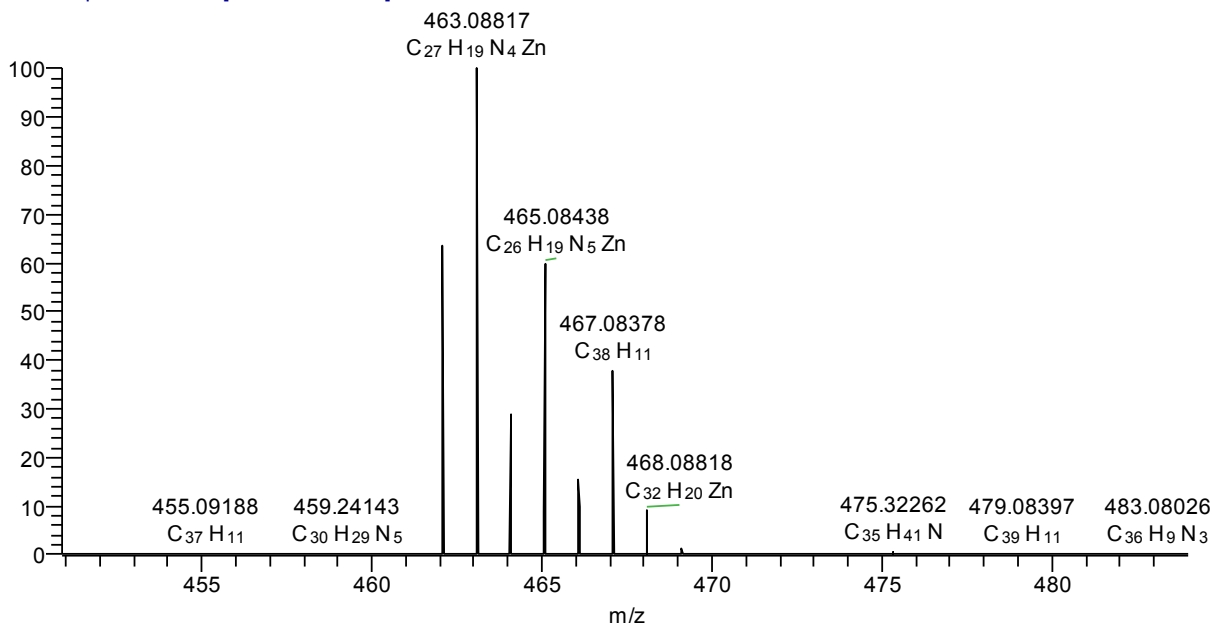


HRMS (ESI) of **5,10-Di-*p*-tolylporphyrin(2c)**

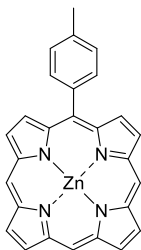




130668 #43-77 RT: 0.24-0.42 AV: 35 NL: ...  
T: FTMS + p ESI Full ms [150.00-1000.00]

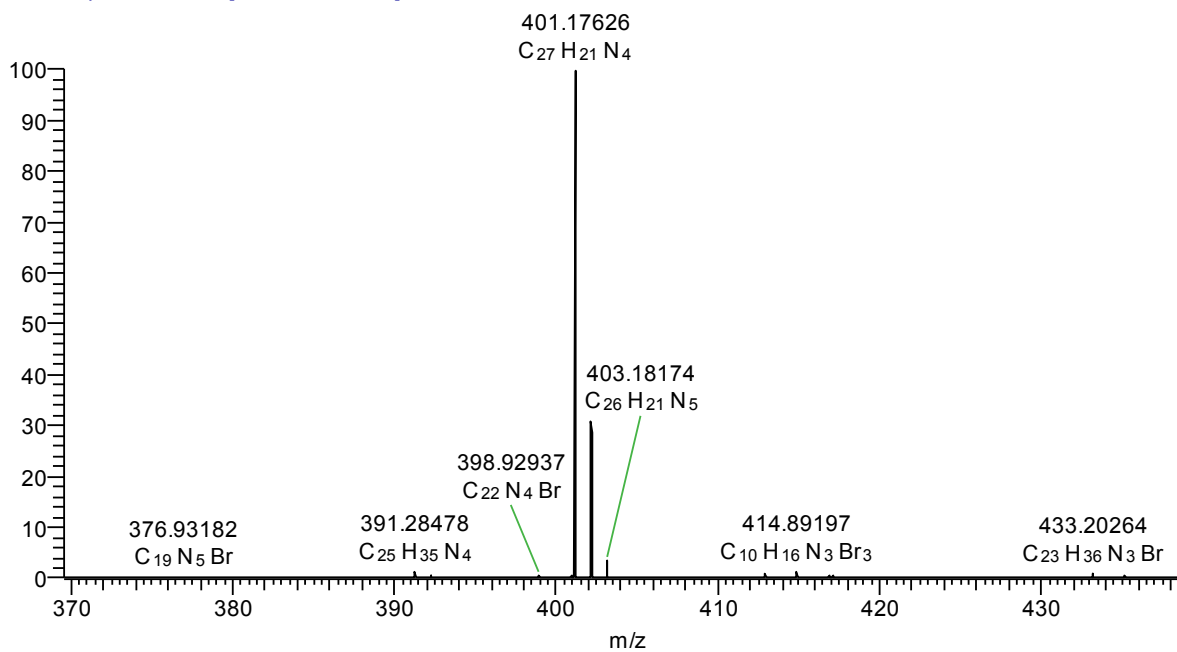


### HRMS (ESI) of Zn(II)-5-*p*-tolylporphyrin (Zn3)

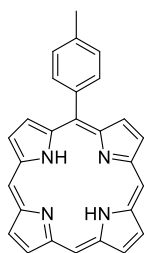


Chemical Formula: C<sub>27</sub>H<sub>18</sub>N<sub>4</sub>Zn  
Exact Mass: 462.08229

130669 #110-130 RT: 0.59-0.70 AV: 21 NI  
T: FTMS + p ESI Full ms [150.00-1000.00]

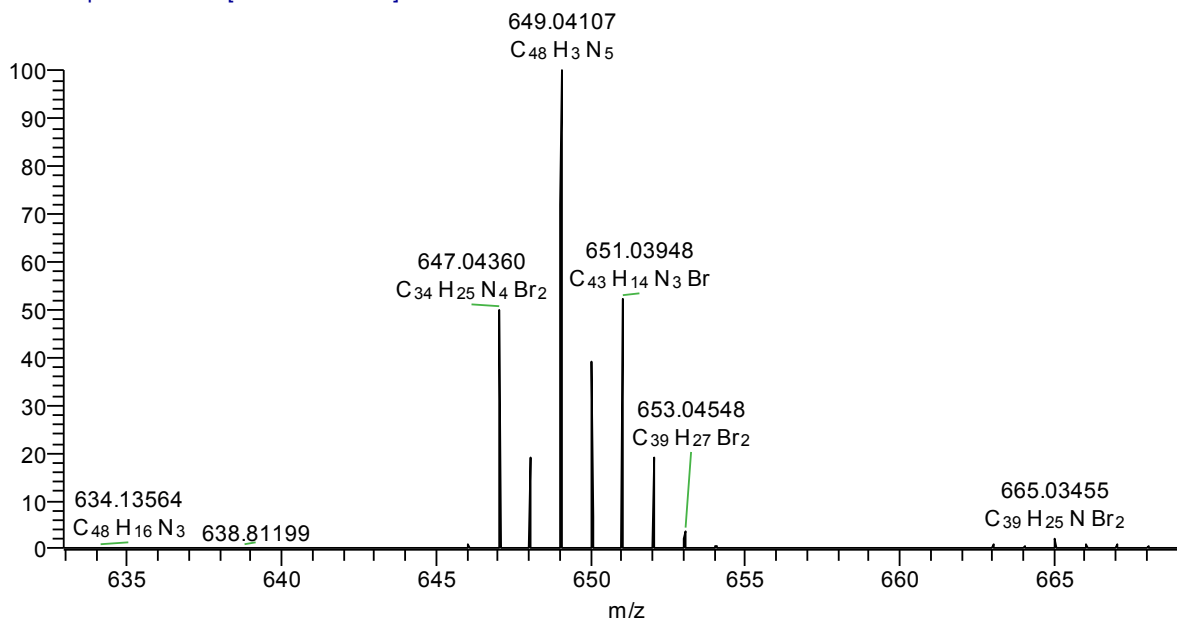


### HRMS (ESI) of 5-*p*-tolylporphyrin (3)

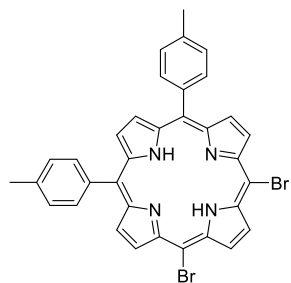


Chemical Formula: C<sub>27</sub>H<sub>20</sub>N<sub>4</sub>  
Exact Mass: 400.16880

130667 #148-171 RT: 0.78-0.90 AV: 24 I  
T: FTMS + p ESI Full ms [150.00-1000.00] iE7

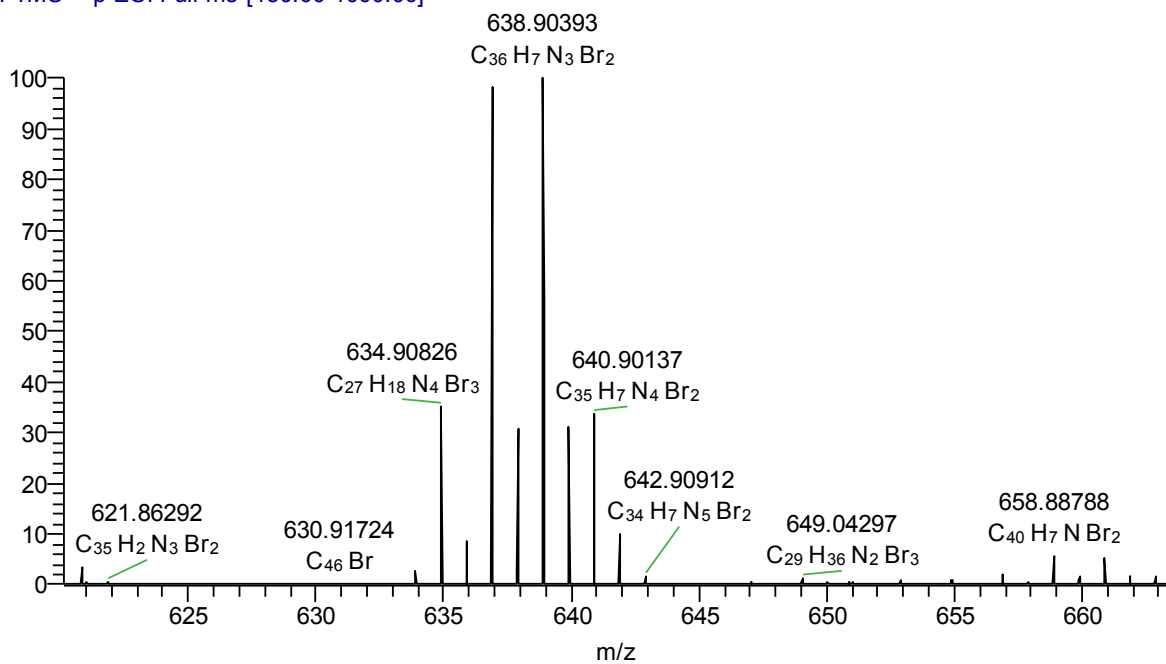


HRMS (ESI) of 5,10-Dibromo-15,20-di-*p*-tolylporphyrin (2-Br<sub>2</sub>C)

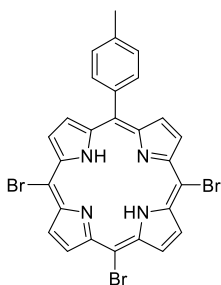


Chemical Formula: C<sub>34</sub>H<sub>24</sub>Br<sub>2</sub>N<sub>4</sub>  
Exact Mass: 646.03677

130670 #216 RT: 1.19 AV: 1 NL: 8.22E6  
T: FTMS + p ESI Full ms [150.00-1000.00]

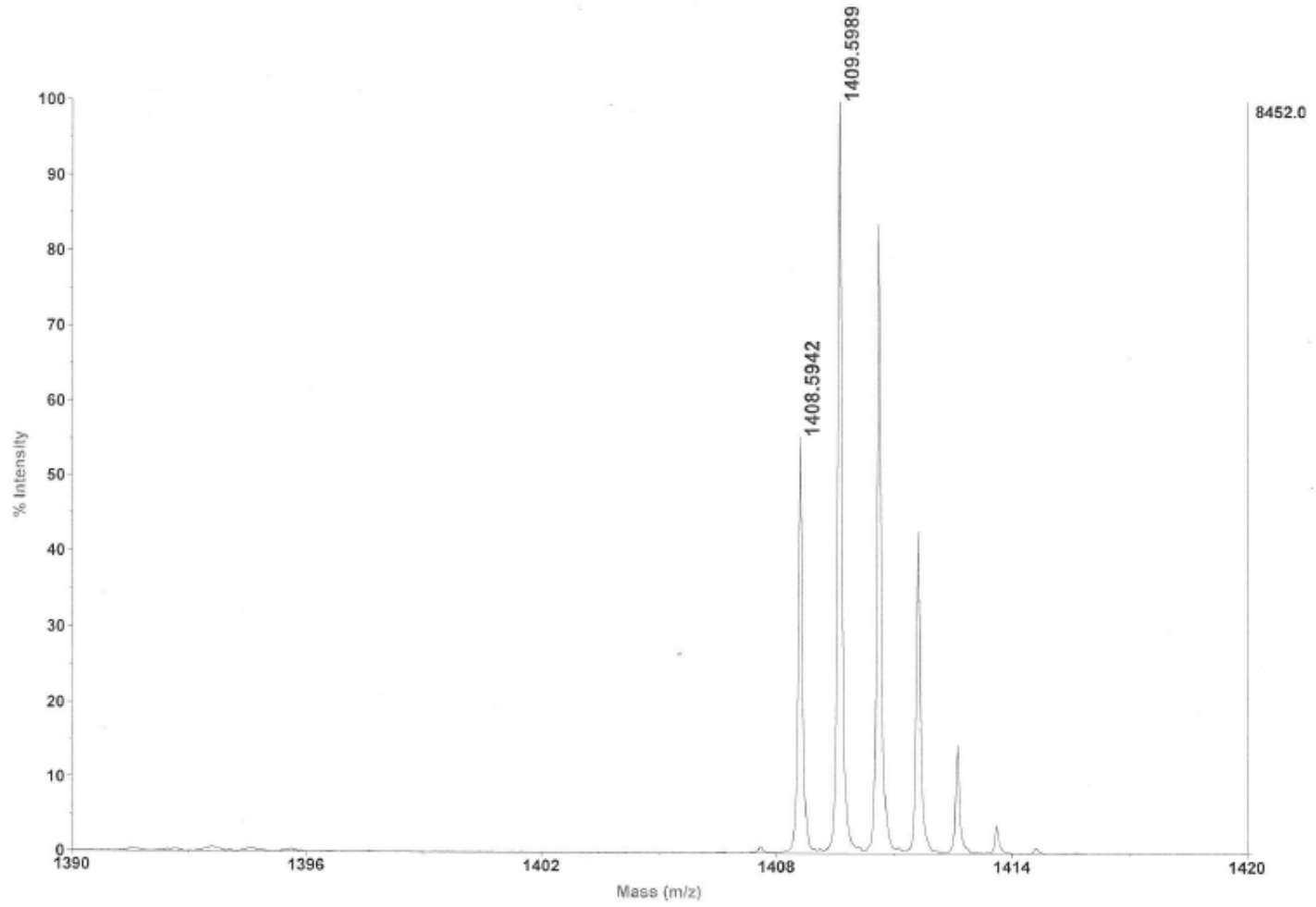


### HRMS (ESI) of 5,10,15-Tribromo-20-*p*-tolylporphyrin (3-Br<sub>3</sub>)



Chemical Formula: C<sub>27</sub>H<sub>17</sub>Br<sub>3</sub>N<sub>4</sub>  
Exact Mass: 633.90033

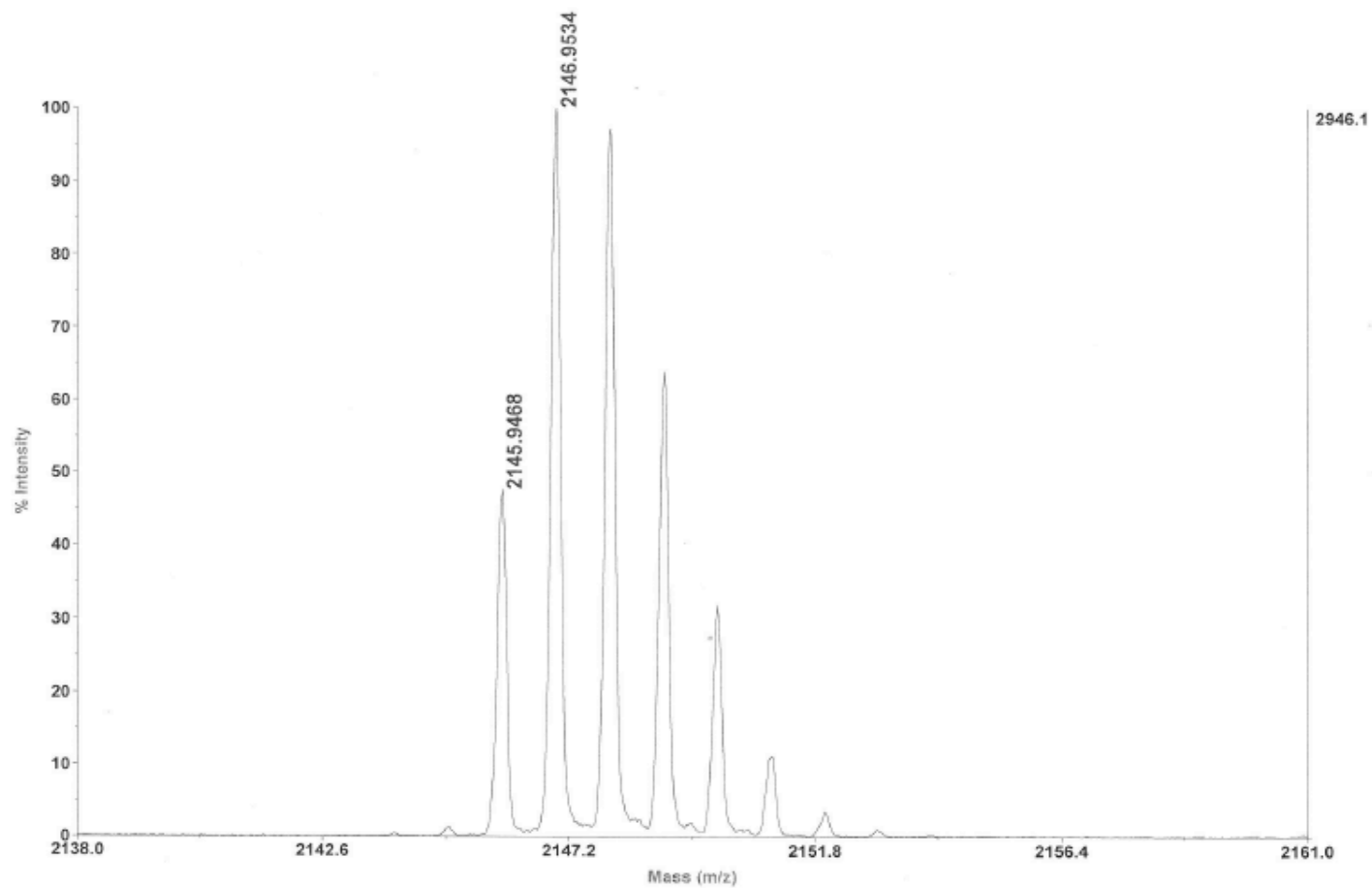
TOF/TOF™ Reflector Spec #1 MC[BP = 365.0, 9824]



MALDI-MS of **PMI<sub>1</sub>P**

AB Sciex TOF/TOF™ Series Explorer™ 72098

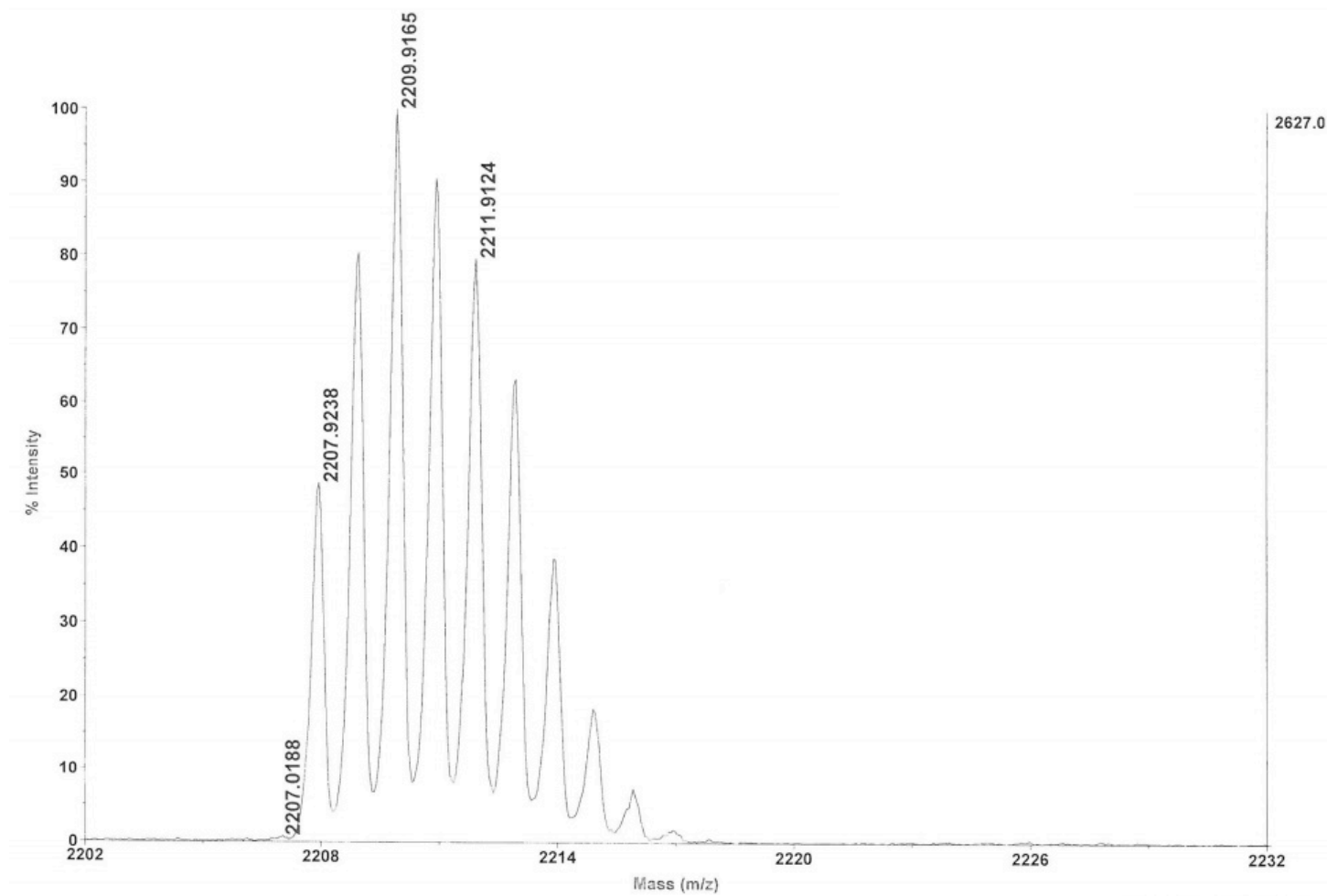
TOF/TOF™ Reflector Spec #1 MC[BP = 364.9, 14906]



MALDI-MS of  $\text{PMI}_{2T}\text{P}$

AB Sciex TOF/TOF™ Series Explorer™ 72098

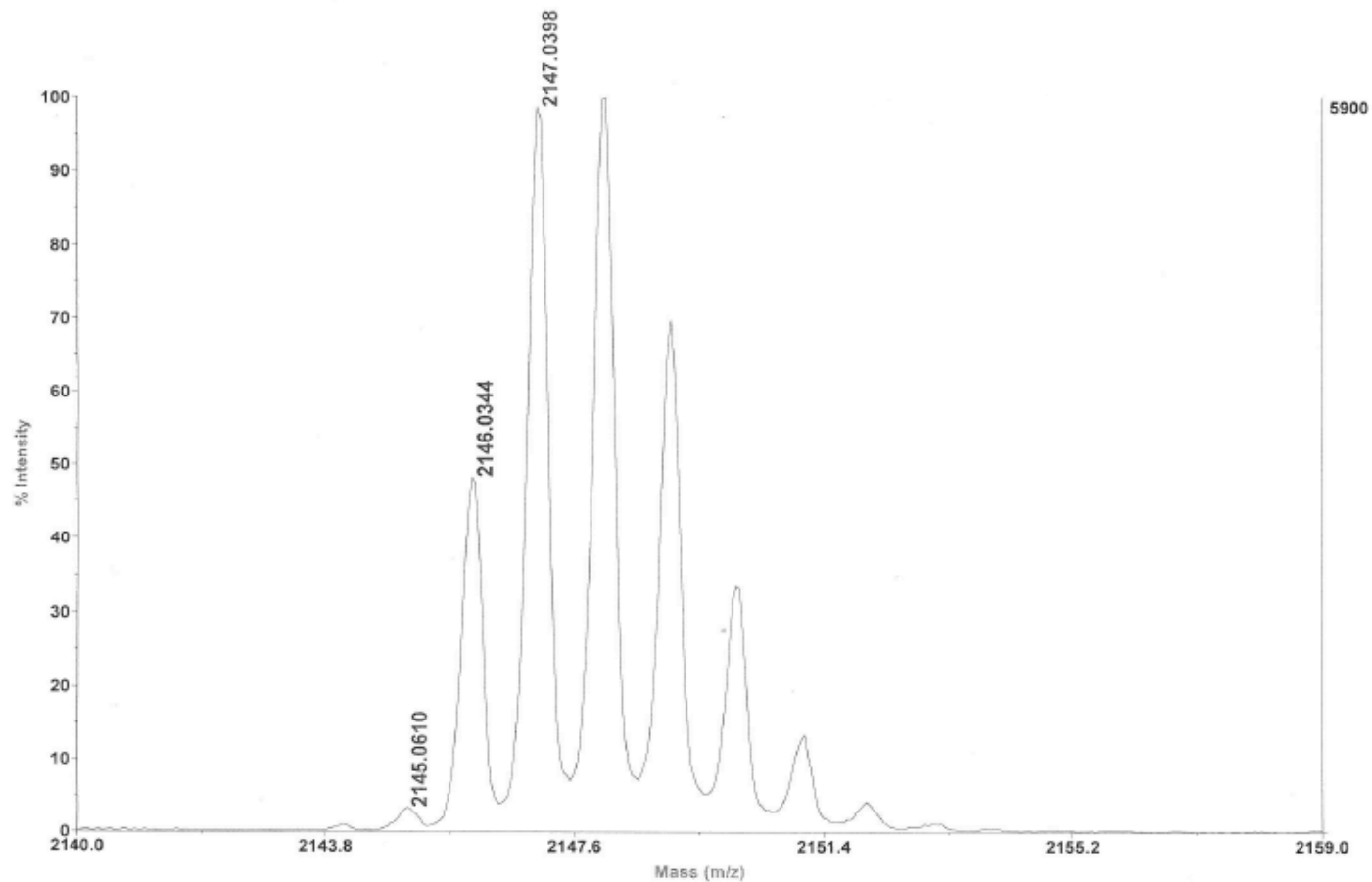
TOF/TOF™ Reflector Spec #1 MC[BP = 365.0, 11443]



MALDI-MS of  $\text{PMI}_2\text{CZnP}$

AB Sciex TOF/TOF™ Series Explorer™ 72098

TOF/TOF™ Reflector Spec #1 MC[BP = 365.0, 19946]

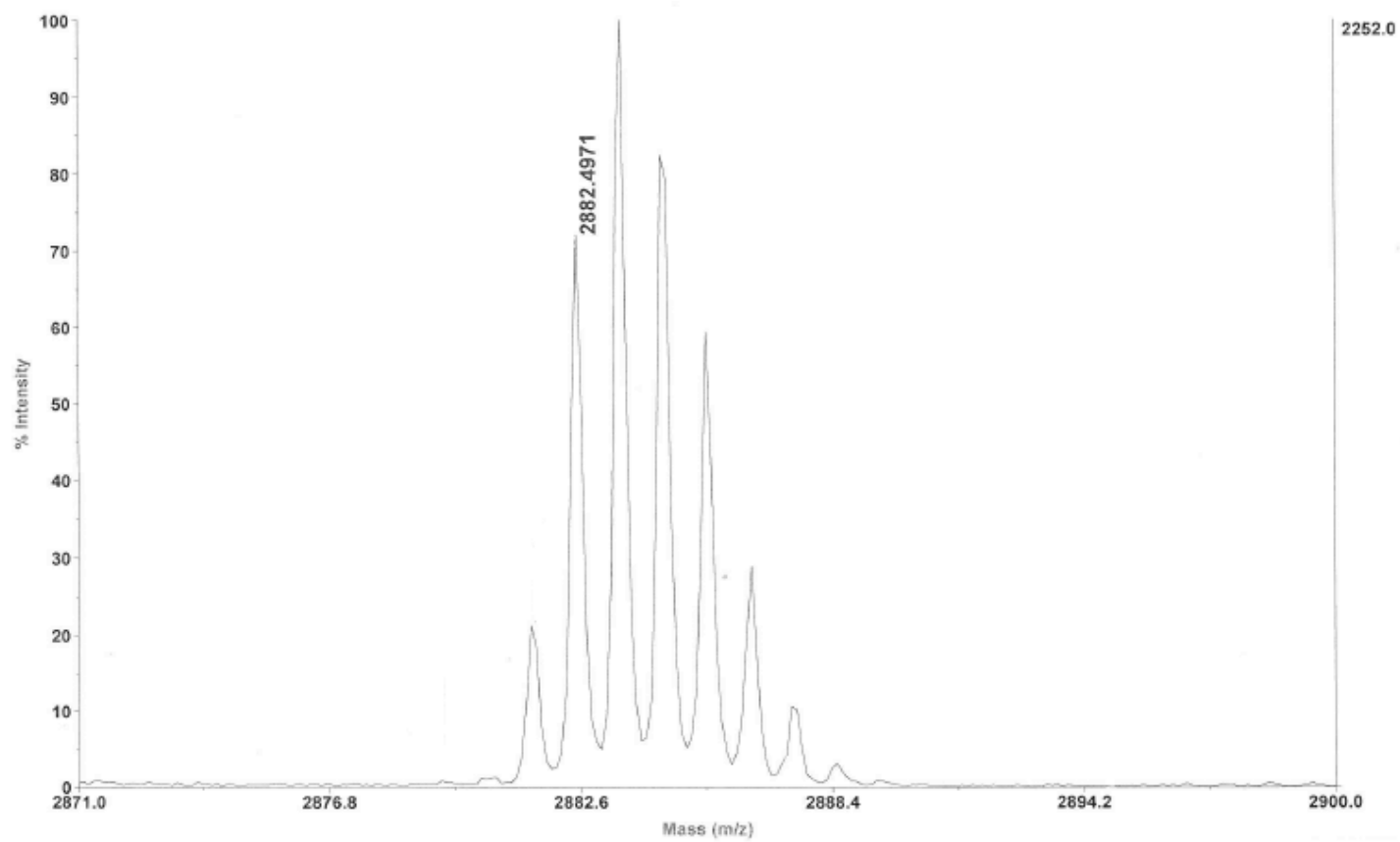


MALDI-MS of  $\text{PMI}_2\text{cP}$



AB Sciex TOF/TOF™ Series Explorer™ 72098

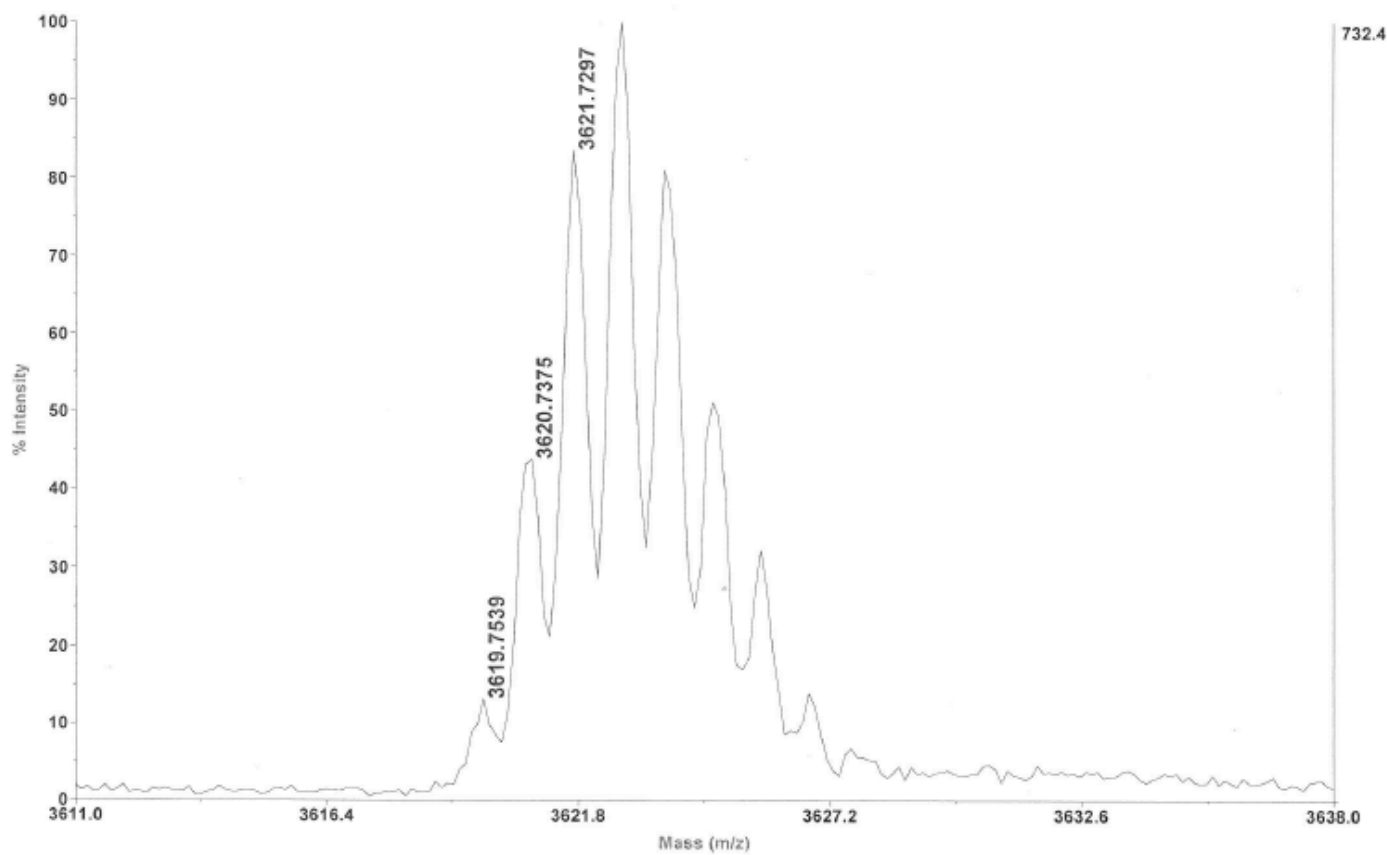
TOF/TOF™ Reflector Spec #1 MC[BP = 2883.5, 2252]



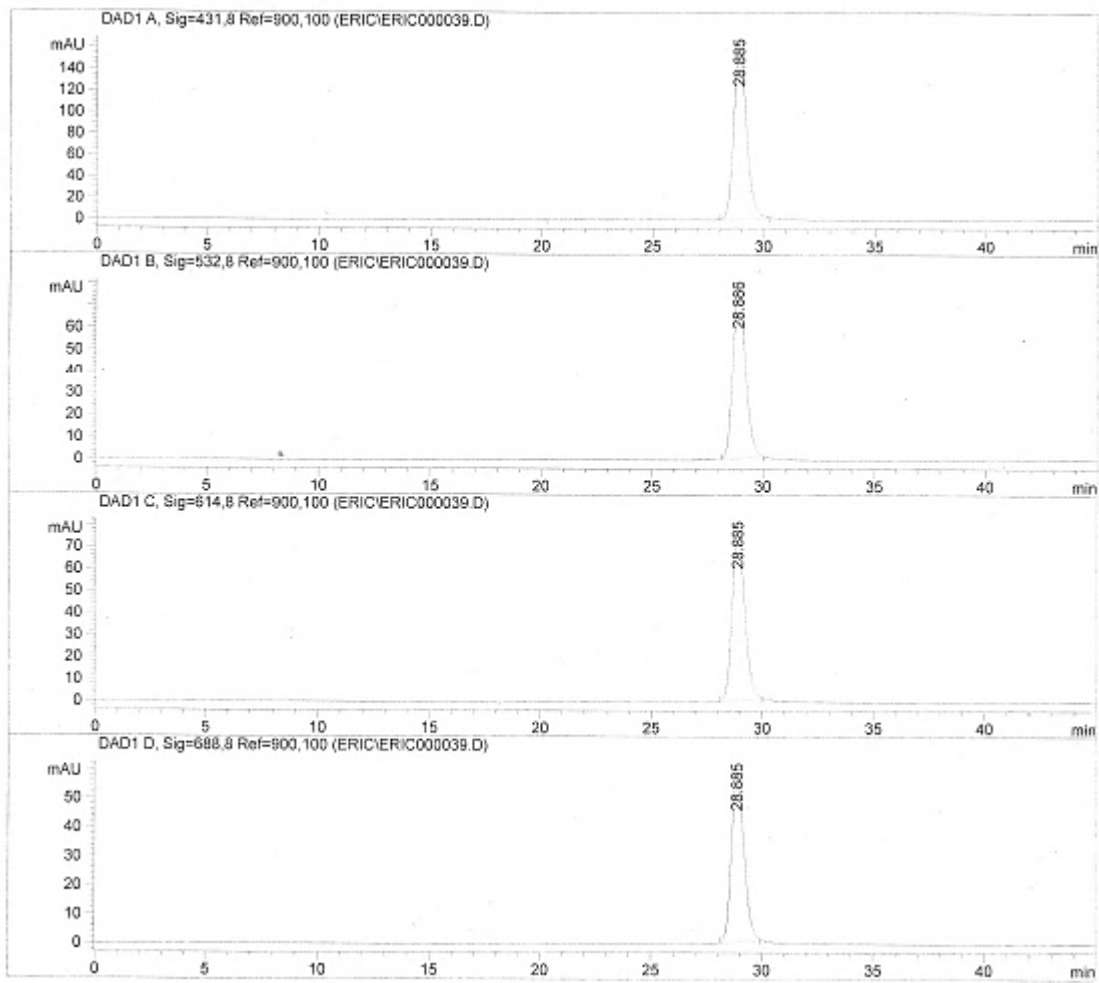
MALDI-MS of  $\text{PMI}_3\text{P}$

AB Sciex TOF/TOF™ Series Explorer™ 72098

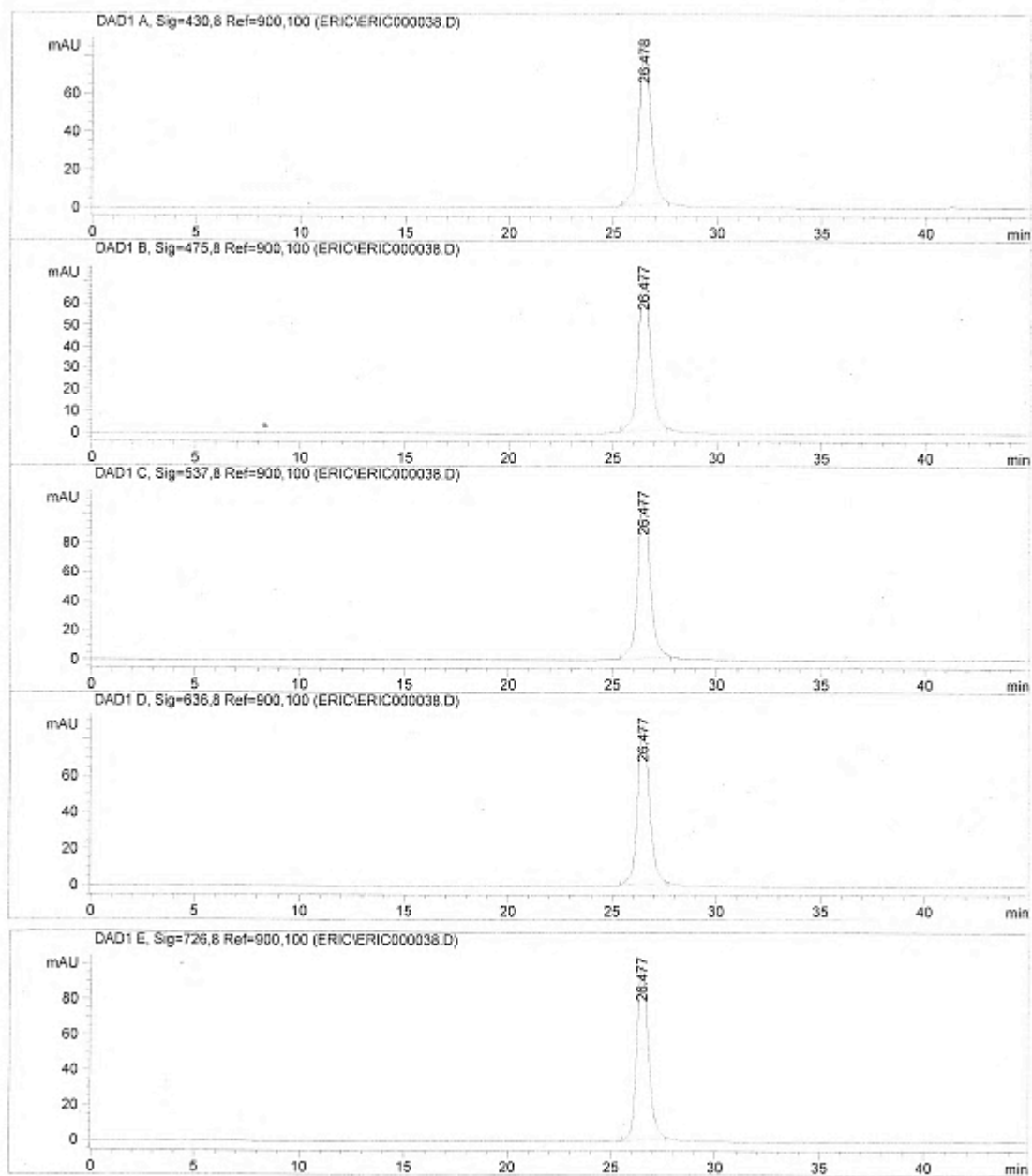
TOF/TOF™ Reflector Spec #1 MC[BP = 3622.7, 732]



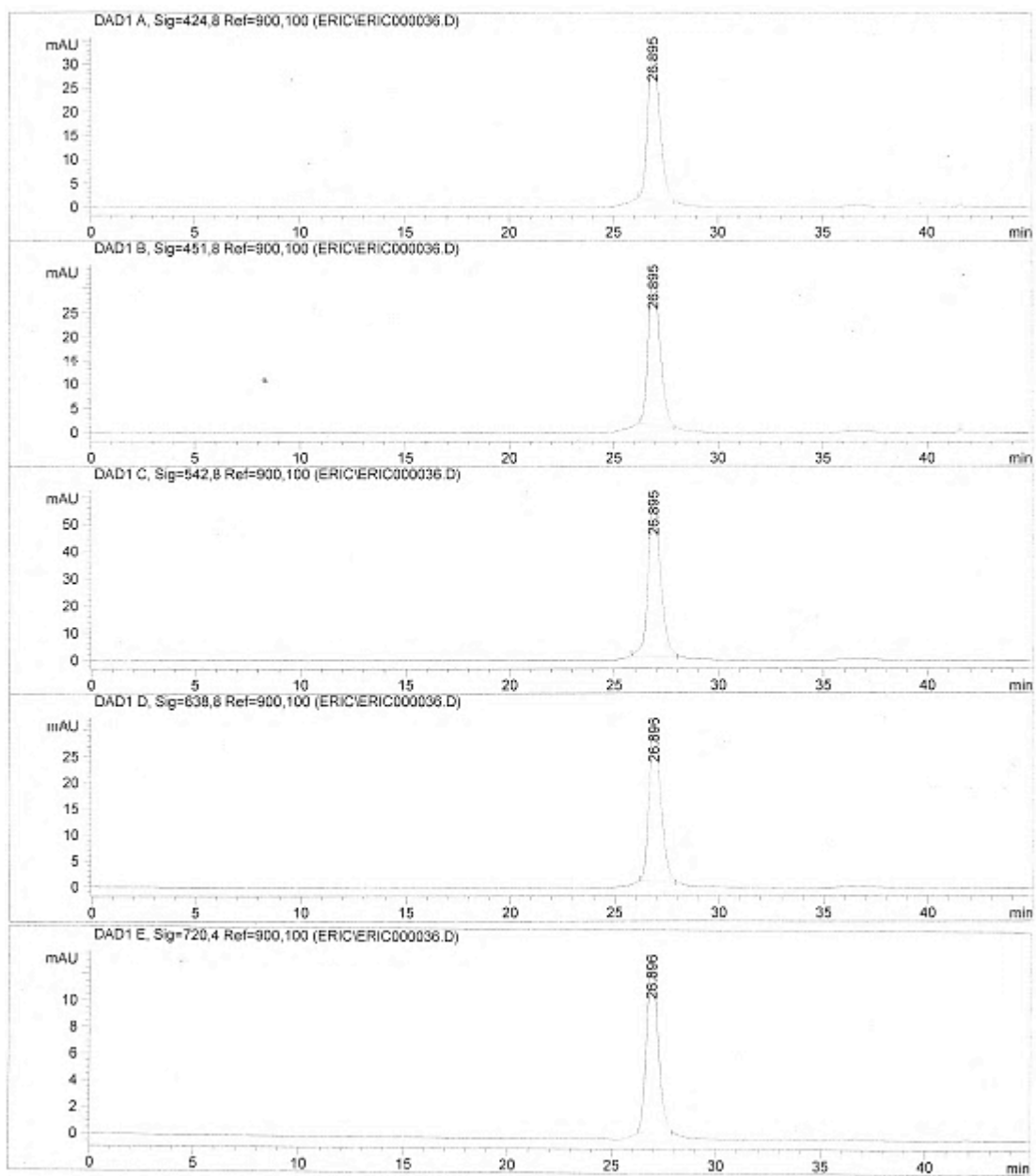
MALDI-MS of **PMI<sub>4</sub>P**



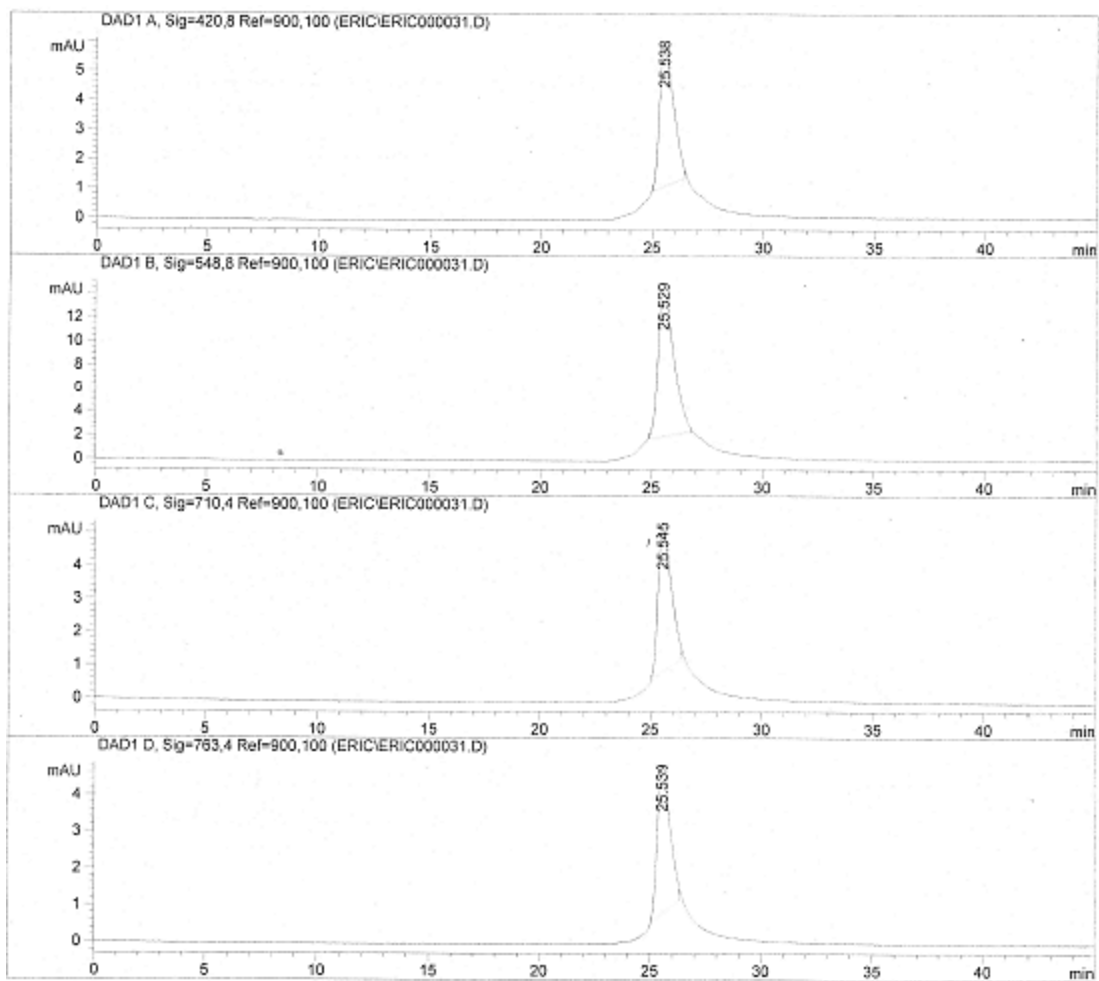
SEC-HPLC traces of **PMI<sub>1</sub>P**



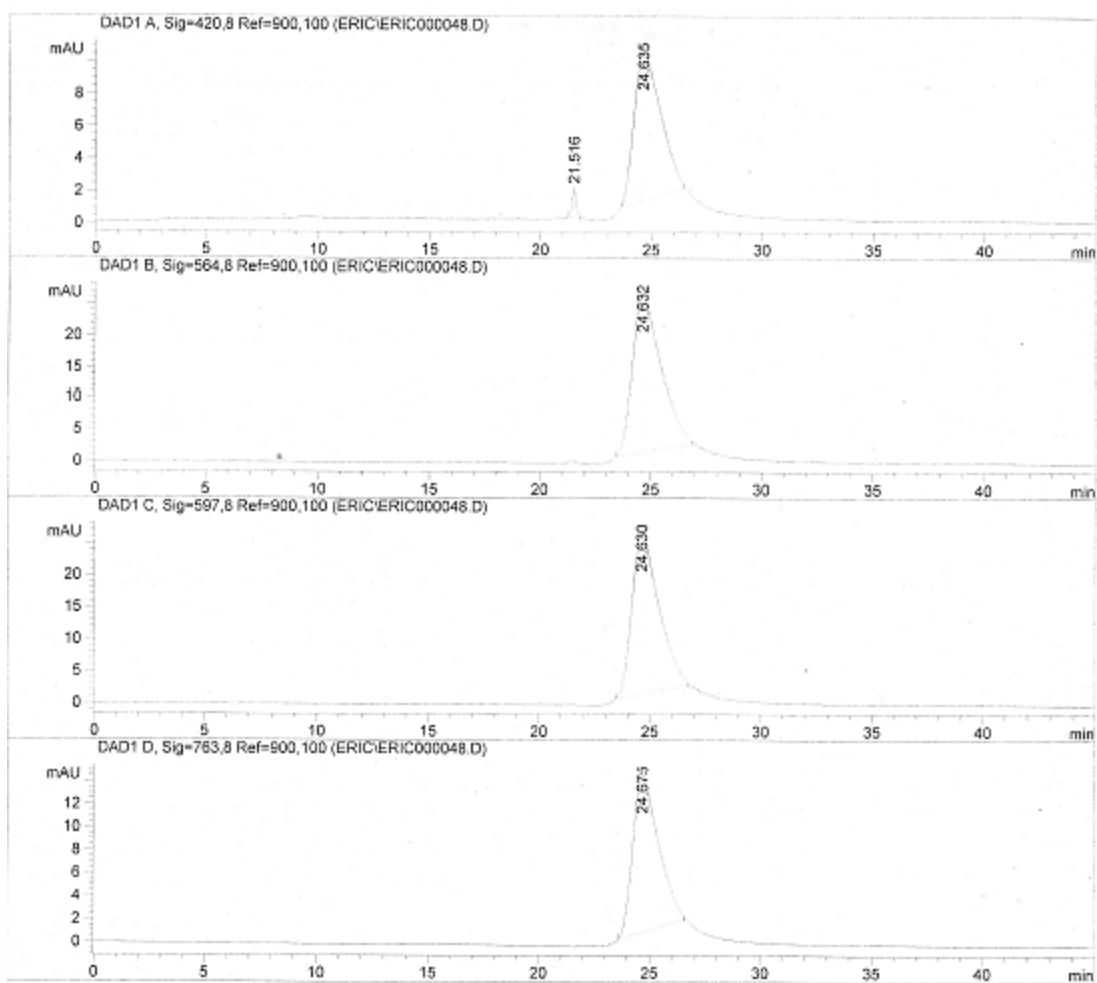
SEC-HPLC traces of **PMI<sub>2</sub>T<sub>P</sub>**



SEC-HPLC traces of **PMI<sub>2</sub>C P**



SEC-HPLC traces of  $\text{PMI}_3\text{P}$



SEC-HPLC traces of **PMI<sub>4</sub>P**