Straightforward and Relatively Safe Process for the Fluoride Exchange of Trivalent and Tetravalent, Group 13 and 14 Phthaloecyanines.

Electronic Supporting Information.

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**Table S1.5:** Solubilities of fluoride salts, chloride salts, bromide salts, and iodide salts in $N, N$-dimethylacetamide (DMAc) and dimethyl sulfoxide (DMSO)

**Table S2.** UV-Vis absorbance spectroscopy results for chloro and fluoro group 13 and group 14 metal containing Pcs.

**Table S3.** Electrochemical characterization of the chloro and fluoro derivatives of the aluminum, gallium, silicon and germanium containing Pcs.
| Salts | Source | Solubility (g/kg) | Br/Cl Ratio | I/Cl Ratio | Salts | Source | Solubility (g/kg) | Br/Cl Ratio | I/Cl Ratio |
|-------|--------|------------------|-------------|------------|-------|--------|------------------|-------------|------------|
| LiCl  | Not Available | LiCl | Dawson | 18.2396 | - | - |
| LiBr  | Not Available | LiBr | Not Available | - | - |
| NaF   | Not Available | NaF | Not Available | - | - |
| NaCl  | Burgess | 24.5 | - | - | NaCl | Chandra | 20.5 | - | - |
| NaBr  | Menschutkin | 280.0 | 11.4 | - | NaBr | Chandra | 190.8 | 9.3 | - |
| NaI   | Sarkisov | 359.0 | - | 14.7 | NaI | Chandra | 514.8 | - | 25.1 |
| KCl   | Wallace | 24.5 | - | - | KCl | Chandra | 8.7 | - | - |
| KBr   | Wallace | 103.0 | 4.2 | - | KBr | Chandra | 47.7 | 5.52 | - |
| KI    | Wallace | 323.0 | - | 13.2 | KI | Chandra | 304.3 | - | 35.2 |
| RbBr  | Not Available | RbBr | Not Available | - | - |
| CsCl  | Not Available | CsCl | Not Available | - | - |
| CsBr  | Not Available | CsBr | Not Available | - | - |
| CsI   | Not Available | CsI | Not Available | - | - |
| MgCl₂ | Not Available | MgCl₂ | Not Available | - | - |
| CaCl₂ | Menschutkin | 253.0 | - | - | CaCl₂ | Dawson | 30.0 | - | - |
| CaBr₂ | Not Available | CaBr₂ | Dawson | 80.0 | 2.7 | - |
| SrCl₂ | Not Available | SrCl₂ | Chandra | 161.3 | - | - |
| SrBr₂ | Not Available | SrBr₂ | Chandra | 415.0 | 2.6 | - |
| BaCl₂ | Not Available | BaCl₂ | Chandra | 124.7 | - | - |
| BaBr₂ | Not Available | BaBr₂ | Chandra | 385.0 | 3.1 | - |

**Table S1.1**: Solubilities of fluoride salts, chloride salts, bromide salts, and iodide salts in acetamide and N-methylacetamide [1-11].
| Salts | Source | Solubility (g/kg) | Br/Cl Ratio | I/Cl Ratio | Salts | Source | Solubility (g/kg) | Br/Cl Ratio | I/Cl Ratio |
|-------|--------|------------------|-------------|------------|-------|--------|------------------|-------------|------------|
| LiCl  | Paul and Berardelli | 266.5 | - | - | LiCl  | Paul, Starck & Berardelli | 230.0 | - | - |
| LiBr  | Paul and Berardelli | 596.5 | **2.2** | - | LiBr  | Paul and Berardelli | 446.0 | **1.9** | - |
| NaF   | Colton | 1.0 | - | - | NaF   | Not Available | |
| NaCl  | Paul, Berardelli, and Gopal | 92.2 | - | - | NaCl  | Berardelli and Strack | 32.6 | - | - |
| NaBr  | Paul, Berardelli, and Gopal | 353.4 | **3.8** | - | NaBr  | Paul, Strack & Berardelli | 298.0 | **9.2** | - |
| NaI   | Paul and Gopal | 600.0 | - | **6.5** | NaI   | Paul & Strack | 787.0 | - | **24.2** |
| KCl   | Paul, Berardelli, Gopal, and Pavlopolpus | 62.3 | - | - | KCl   | Paul, Strack & Berardelli | 22.4 | - | - |
| KBr   | Paul, Berardelli, and Gopal | 215.3 | **3.5** | - | KBr   | Paul, Strack & Berardelli | 101.5 | **4.5** | - |
| KI    | Paul, Berardelli, Gopal, Colton, and Pavlopolpus | 683.0 | - | **11.0** | KI    | Berardelli and Strack | 491.0 | - | **21.9** |
| RbBr  | Pavlopolpus | 274.5 | - | - | RbBr  | Not Available | |
| CsCl  | Alexander | 91.5 | - | - | CsCl  | Not Available | |
| CsBr  | Alexander | 152.4 | **1.7** | - | CsBr  | |
| CsI   | Alexander and Pavlopolous | 315.2 | - | **3.4** | CsI   | |
| MgCl₂ | Berardelli | 84.0 | - | - | MgCl₂ | Berardelli | 88.0 | - | - |
| CaCl₂ | Berardelli, Gopal, and Colton | 202.0 | - | - | CaCl₂ | Berardelli | 186.0 | - | - |
| CaBr₂ | Berardelli | 434.0 | **2.2** | - | CaBr₂ | Berardelli | 303.0 | **1.6** | - |
| SrCl₂ | Gopal | 156.9 | - | - | SrCl₂ | Not Available | |
| SrBr₂ | Gopal | 190.5 | **1.2** | - | SrBr₂ | |
| BaCl₂ | Gopal | 117.6 | - | - | BaCl₂ | Not Available | |
| BaBr₂ | Gopal | 305.0 | **2.6** | - | BaBr₂ | |

**Table S1.2:** Solubilities of fluoride salts, chloride salts, bromide salts, and iodide salts in formamide and N-methylformamide [1-11].
Table S1.3: Solubilities of fluoride salts, chloride salts, bromide salts, and iodide salts in acetonitrile [1-11].
### Table S1.4: Solubilities of fluoride salts, chloride salts, bromide salts, and iodide salts in N,N-dimethylformamide (DMF) [1-11].

| Salts   | Source         | Solubility (g/kg) | Br/Cl Ratio | Br/Cl Ratio | I/Cl Ratio | I/Cl Ratio |
|---------|----------------|-------------------|-------------|-------------|------------|------------|
| CsI     | Kellogg, R.M   | 38.3              | -           | -           | 74.5       | -          |
| CsBr    | Kellogg, R.M   | 5.4               | 10.8        | -           | -          | -          |
| CsCl    | Kellogg, R.M   | 0.5               | -           | -           | -          | -          |
| CsF     | Kellogg, R.M   | 0.1               | -           | -           | -          | -          |
| KI      | Kellogg, R.M   | 271.1             | -           | -           | 542.3      | 1,500.6    |
| KI      | Flick, Ernest W.| 250.0             | -           | -           | 500.0      | 1,383.7    |
| KBr     | Labban and Marcus | 9.1               | 18.2        | 50.4        | -          | -          |
| KBr     | Kellogg, R.M   | 8.2               | 16.3        | 45.1        | -          | -          |
| KCl     | Flick, Ernest W.| 0.5               | -           | -           | -          | -          |
| KCl     | Kellogg, R.M   | 0.2               | -           | -           | -          | -          |
| KF      | Kellogg, R.M   | 0.1               | -           | -           | -          | -          |
| NaI     | Flick, Ernest W.| 144.0             | -           | -           | 288.0      | 403.2      |
| NaI     | Kellogg, R.M   | 79.0              | -           | -           | 158.0      | 221.1      |
| NaBr    | Kellogg, R.M   | 117.1             | 234.2       | 327.8       | -          | -          |
| NaCl    | Flick, Ernest W.| 0.5               | -           | -           | -          | -          |
| NaCl    | Kellogg, R.M   | 0.4               | -           | -           | -          | -          |
| NaF     | Kellogg, R.M   | 0.1               | -           | -           | -          | -          |
| LiI     | Not Available  |                   |             |             |            |            |
| LiBr    | Kellogg, R.M   | 206.8             | 1.8         | -           | -          | -          |
| LiCl    | Flick, Ernest W.| 114.0             | -           | -           | -          | -          |
| LiF     | Kellogg, R.M   | 0.1               | -           | -           | -          | -          |
| Salts  | Source            | Solubility (g/kg) | Br/Cl Ratio | I/Cl Ratio | Source            | Solubility (g/kg) | Br/Cl Ratio | I/Cl Ratio |
|--------|-------------------|-------------------|-------------|------------|-------------------|-------------------|-------------|------------|
| CsI    | Not Available     |                   |             |            | CsI               |                   |             |            |
| CsBr   |                   |                   |             |            | CsBr              |                   |             |            |
| CsCl   |                   |                   |             |            | CsCl              |                   |             |            |
| CsF    |                   |                   |             |            | CsF               |                   |             |            |
| KI     | Pistoia & Scrosati | 15.4              | -           | 140.0      | KI                | 181.7             | -           | 100.0      |
| KBr    | Pistoia & Scrosati | 3.9               | 35.5        | -          | KBr               | 59.0              | 32.5        | -          |
| KCl    | Pistoia & Scrosati | 0.1               | -           | -          | KCl               | 1.8               | -           | -          |
| KF     | N/A               |                   |             |            | KF                |                   |             |            |
| NaI    | Pistoia & Scrosati | 346.0             | -           | 1,730.0    | NaI               | 272.5             | -           | 75.0       |
| NaBr   | Pistoia & Scrosati | 65.1              | 325.5       | -          | NaBr              |                   |             |            |
| NaCl   | Pistoia & Scrosati | 0.2               | -           | -          | NaCl              | 3.6               | -           | -          |
| NaF    | N/A               |                   |             |            | NaF               |                   |             |            |
| LiI    | Fedorov           | 45.6              | -           | 0.5        | LiI               | 373.3             | -           | 4.0        |
| LiBr   | Pistoia & Scrosati | 262.0             | 3.1         | -          | LiBr              | 285.2             | 3.1         | -          |
| LiCl   | Pistoia & Scrosati | 86.0              | -           | -          | LiCl              | 92.6              | -           | -          |
| LiF    | N/A               |                   |             |            | LiF               |                   |             |            |

Table S1.5: Solubilities of fluoride salts, chloride salts, bromide salts, and iodide salts in \(N,N\)-dimethylacetamide (DMAc) and dimethyl sulfoxide (DMSO) [1-11].
Table S2. UV-Vis absorbance spectroscopy results for chloro and fluoro group 13 and group 14 metal containing Pcs.

| Sample         | DMSO | Chloroform | Toluene |
|----------------|------|------------|---------|
|                | $\lambda_{\text{max}}$ (nm) | Egap (eV) | $\lambda_{\text{max}}$ (nm) | Egap (eV) | $\lambda_{\text{max}}$ (nm) | Egap (eV) |
| Cl-AlPc        | 680  | 1.78       | 681     | 1.77       | 688     | 1.77       |
| F-AlPc         | 671  | 1.81       | 688     | 1.77       | 690     | 1.76       |
| Cl-GaPc        | 678  | 1.79       | 687     | 1.77       | 687     | 1.77       |
| F-GaPc         | 676  | 1.79       | 687     | 1.77       | 686     | 1.78       |
| Cl$_2$-SiPc    | 700  | 1.73       | 694     | 1.75       | 685     | 1.77       |
| F$_2$-SiPc     | 699  | 1.73       | 694     | 1.75       | 726     | 1.67       |
| Cl$_2$-GePc    | 677  | 1.78       | 679     | 1.78       | 691     | 1.76       |
| F$_2$-GePc     | 680  | 1.77       | 689     | 1.77       | 678     | 1.79       |
**Table S3.** Electrochemical characterization of the chloro and fluoro derivatives of the aluminum, gallium, silicon and germanium containing Pcs.

| Sample   | $E_{OX, peak}$ (V) | $E_{Red, peak}$ (V) | $E_{OX, 1/2}$ (V) | $E_{Red, 1/2}$ (V) | $\Phi_{XPS}$ (eV) | $\Phi_{UPS}$ (eV) | $E_{HOMO,UPS}$ (eV) |
|----------|--------------------|----------------------|-------------------|-------------------|------------------|------------------|---------------------|
| Cl-AlPc  | 1.40*              | -0.71*, -0.96*, -1.40| -                 | -                 | 4.5              | 4.4              | 5.7                 |
| F-AlPc   | 1.18*              | -0.81, -1.35*        | -                 | -0.74, -          | 4.4              | 3.6              | 4.7                 |
| Cl-GaPc  | 0.91, 1.27         | -0.79*, -1.19        | 0.88, 1.24        | -                 | 4.4              | 4.3              | 5.7                 |
| F-GaPc   | 1.19*              | -0.74                | -                 | -0.69             | 4.4              | 4.3              | 5.6                 |
| Cl$_2$-SiPc | 1.27*          | -0.68, -1.07         | -                 | -0.62, -1.02      | 4.1              | 4.1              | 5.7                 |
| F$_2$-SiPc | 1.23              | -0.63                | 1.13              | -0.60             | 4.1              | 4.0              | 5.6                 |
| Cl$_2$-GePc | 1.39*           | -0.75*               | -                 | -                 | 4.5              | 4.4              | 5.8                 |
| F$_2$-GePc | 1.28*            | -0.86*               | -                 | -                 | 4.1              | 4.1              | 4.3                 |

*Denotes that the peak was irreversible.
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