



**Stimuli-Responsive Chromism in Organophosphorus  
Chemistry**

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## Stimuli-Responsive Chromism in Organophosphorus Chemistry

Christian Reus<sup>a</sup> and Thomas Baumgartner<sup>\*a</sup>Received 00th January 20xx,  
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Changes in color are one of the most obvious and easily followed responses that can be induced by an external stimulus.  $\pi$ -Conjugated organophosphorus compounds are on the rise to challenge established systems by opening up new and simple pathways to diversely modified optoelectronic properties – the main challenge for the development of new chromic materials. Relevant stimuli highlighted in this Frontier article include electronic current (electrochromism), light (photochromism), solvent polarity (solvatochromism), aggregation formation (aggregation induced emission, AIE), mechanical force (mechanochromism), temperature (thermochromism), organic solvent vapor (vapochromism), and pH (halochromism).

### Introduction

Visual perception is the most important sense available to humans for gathering information about their environment. Therefore, the color of objects plays an elemental role in everyday life because any changes can easily be discerned with the naked eye or with the help of simple spectrophotometric methods. The range of possible applications for observing a color change widens significantly, if it could be connected to an external chemical or physical stimulus such as pH or light. Corresponding chromic ‘smart’ materials are thus vigorously sought-after for diverse applications reaching from self-dimming glasses for lenses or windows, over thermochromic paints, to state-of-the-art displays.<sup>1</sup>

An ever-growing number of organic  $\pi$ -conjugated systems are employed as such smart materials by adjusting their electronic structures to meet the desired requirements. Implementing phosphorus centers into conjugated frameworks has recently paved the way for carrying out these modifications in an easy and effective way. Phospholes show particularly promising optoelectronic features due to a significantly lowered energy level of the Lowest Unoccupied Molecular Orbital (LUMO) which results from an efficient phosphorus-centered  $\sigma^*-\pi^*$  hyperconjugation.<sup>2</sup>

The development of phosphorus-based materials has rapidly gained traction in recent years and already led to applications of functional phospholes in organic electronics such as organic light-emitting devices<sup>3</sup> or photovoltaics.<sup>4</sup> This trend is also obvious from an increasing number of review articles on this topic.<sup>5</sup> To complement these reviews, this Frontier article now focuses on representative research published within the last five years that reports various forms of stimuli-responsive

chromism in the field of organophosphorus chemistry, to highlight the tremendous practical value of such species and potential applications for the materials.

### Discussion

#### Electrochromism. Stimulus: electronic current

The process of a color change upon an oxidative or reductive electron transfer is known as electrochromism and is typically reversible, if the electron transfer is reversible.<sup>1</sup> In 2011, our group has presented the first phosphorus-based molecules that exhibit this behavior. The framework, into which phosphorus was placed, is known as viologen, a class of  $N,N'$ -diquaternized 4,4'-bipyridines that are well-known for their efficient electrochromism. A spectroelectrochemical analysis of the simplest  $N,N'$ -dimethylated 2,7-diazadibenzophosphole revealed significant changes in the absorption spectrum upon reduction.<sup>6</sup> The potential applicability as electrochromic material was further elaborated in a follow-up study, in which a series of  $N,N'$ -dibenzylated phosphaviologens were

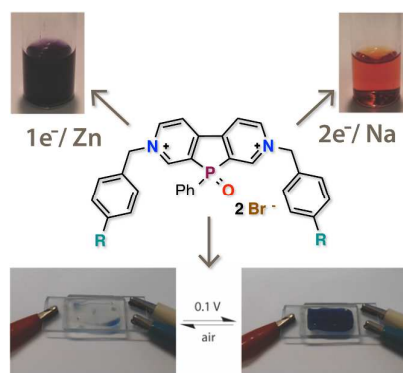


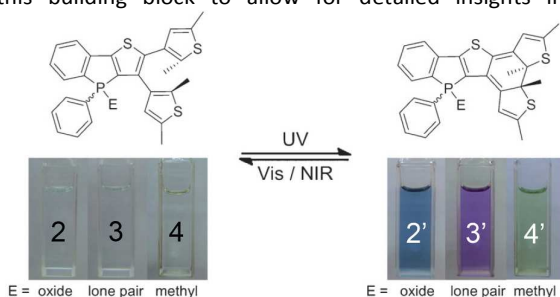
Fig. 1 Electrochromic phosphaviologen 1 (R = H). Reproduced with permission from Ref 7. Copyright (2015) American Chemical Society.

<sup>a</sup> Department of Chemistry and Centre for Advanced Solar Materials, University of Calgary, 2500 University Drive NW, Calgary, Alberta T2N 1N4, Canada. E-mail: Thomas.Baumgartner@ucalgary.ca.

compared.<sup>7</sup> Upon both chemical and electronic reduction, *N,N'*-dibenzyl-2,7-diazadibenzophosphole **1** (Fig. 1, R = H) reversibly switches its color between colorless (dication **1**), blue (radical cation), and orange (neutral; Fig. 1),<sup>7</sup> and the practical utility of **1** was verified in a proof-of-concept electrochromic cell (Fig. 1). Thus, phosphaviologens are capable of competing with viologens but offer a great advantage that is highly beneficial for their utilization in applications such as self-dimming mirrors, displays, or smart windows: Their incorporated phosphole motif furnishes significantly lowered reduction potentials of as much as 0.5 V as opposed to parent viologens.<sup>6,7</sup>

#### Photochromism. Stimulus: irradiation with light

The normally UV-light-induced chemical transformation of a compound into another state with a different absorption spectrum is known as photochromism and can usually be reversed by irradiation with light of a longer wavelength or by heating.<sup>1</sup> The latter process is typically undesired, which is why dithienylethenes (DTEs) and combinations thereof with transition metals are widely used, due to their thermal irreversibility and fatigue resistance. Current research is focused on modifying the  $\pi$ -backbone to fine-tune the electronic and optoelectronic properties. Ragogna and coworkers were the first to achieve this by implementation of a phosphorus atom into a diazadithienylbutadiene structure.<sup>8</sup> After polymerization, a fairly reversible switching from the open to the closed form resulted in the observation of a new signal at  $\lambda_{\text{abs}} = 448$  nm. Shortly thereafter, Yam and coworkers found a way to access a series of fused DTE-benzothienophospholes.<sup>9</sup> The photochromic behavior could easily be influenced by simple chemical modification at the phosphorus center (**2-4**; Fig. 2). Transitions from the open to the closed forms upon irradiation at  $\lambda_{\text{ex}} < 400$  nm are accompanied by strong and easily visible color changes from colorless to blue (**2'**), purple (**3'**), or green (**4'**; Fig. 2). The photocyclizations are quite efficient with conversion rates of 37-69% and can be reversed upon exposure to white light. In a case study, **2** was proven to be photoswitchable also while embedded in a poly(methylmethacrylate) film, and its closed form has a good thermal stability as well as a half-life of 442 days in benzene solution.<sup>9</sup> Inspired by these promising results, the same group subsequently extended the structural diversity of this building block to allow for detailed insights into



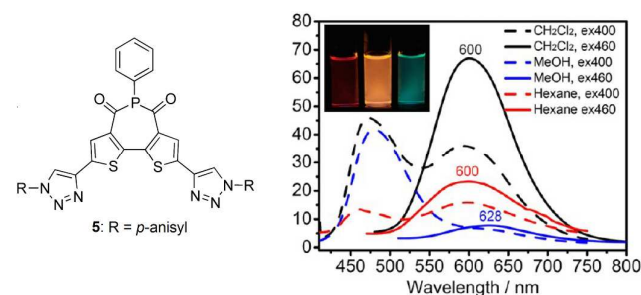
**Fig. 2** Photochromic benzothienophospholes **2-4**. Adapted with permission from Ref 9. Copyright (2013) John Wiley and Sons.

structure-property relationships.<sup>10</sup> While the above-mentioned advantages are secured throughout the modifications, the optoelectronic properties could indeed be fine-tuned so that this study provides an important outlook on future designs of photochromic phospholes.<sup>10</sup> Photochromic materials typically serve as optical switches and memory-storage systems or even security markers as exemplified by the US passport.<sup>1</sup>

#### Solvatochromism. Stimulus: solvent polarity

Whenever a compound switches color upon exposure to an environment with a different polarity – usually an organic solvent but also a gel, micelle, or even different regions in a protein – this phenomenon is called solvatochromism.<sup>1</sup> The observed absorption or emission shifts arise from different polarities in the ground and excited states that are stabilized or destabilized with varying solvents, and can be hypsochromic (negative solvatochromism) or bathochromic in nature (positive solvatochromism). With the development of the dithienophosphole system,<sup>11</sup> which is a relative of the photochromic compounds **2-4**, our group has reported several examples for solvatochromic phospholes that moreover show various other forms of chromism (see below).<sup>12</sup> Especially the substitution of the electron-accepting phosphole unit with electron donors such as diaryl amines led to an efficient intramolecular charge transfer (ICT) in the excited state that is responsible for the observed positive solvatochromism in the emission spectrum.<sup>12</sup>

Another class of solvatochromic organophosphorus compounds developed by us is not based on a phosphole but a diketophosphepin skeleton (e.g. **5**; Fig. 3).<sup>13</sup> The *p*-anisyl substituted derivative **5** is exceptional in that it emits white light in  $\text{CH}_2\text{Cl}_2$  solution resulting from a dual emission at 475 and 600 nm. The reason can be found in its twisted structure in solution and that the lower energy excitation/emission can be attributed to a charge-transfer transition from the peripheral aromatic part to the diketophosphepin core. When **5** is irradiated at  $\lambda_{\text{ex}} = 400$  nm to populate both the low- and high-energy excited states, a special form of solvatochromism is observed: even though the relative positions of the two emission maxima are identical in hexane and  $\text{CH}_2\text{Cl}_2$  solution, the relative intensities of the peaks are different and so are the resulting colors (Fig. 3).<sup>13</sup>



**Fig. 3** Solvatochromic dithienodiketophosphepin **5** and its emission in different solvents. Inset: photograph of emission in hexane,  $\text{CH}_2\text{Cl}_2$ , and MeOH. Adapted with permission from Ref 12. Copyright (2013) American Chemical Society.

Yamaguchi and coworkers described a series of benzophospholes (**6-10**) with very strong solvatochromic responses, from which the donor-substituted phosphole oxide **6** shows best performance regarding its clearly visible color change in solvents of different polarities (Fig. 4).<sup>14,15</sup> Moreover, the hydroxy-substituted compound **10** deserves special mention, because it features not only strong solvatochromism, but also pronounced fluorescence in polar solvents.<sup>15</sup> Quantum chemical calculations suggest an excited-state intramolecular proton transfer (ESIPT) from the hydroxy to the oxide moiety that ultimately leads to non-emissive relaxation to the ground state. Thus, emission occurs only with hydrogen-bonding accepting solvents and the stabilization of the highly polar excited state gives rise to the observed solvatochromism.

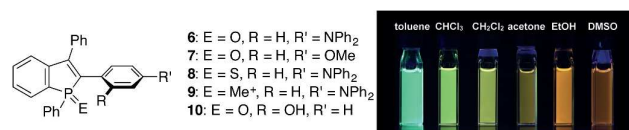


Fig. 4 Solvatochromic benzophospholes **6-10**. Photograph: emission of **6** in different solvents. Adapted with permission from Ref 13. Copyright (2015) John Wiley and Sons.

The technical importance of solvatochromic materials has grown over the last decades as these are important materials for gasoline or polymer characterizations and especially for biological probes and sensors.<sup>1</sup> The latter subject has already been addressed by Yamaguchi *et al.* who presented with **6** the first example of a phosphole-based fluorescent dye that can discriminate between different cellular environments in adipocytes.<sup>14</sup>

#### Aggregation-induced emission (AIE). Stimulus: aggregation

Aggregation-induced emission (AIE) does formally not classify as chromism, since no color change is afforded by aggregation – in that case, it would be called aggregachromism – but a similarly strong optical response can be observed: The fluorescence is either turned "OFF" (no aggregates) or "ON" (aggregation) and thus we include this phenomenon in this Frontier. The AIE effect was originally studied with sterically demanding 2,3,4,5-tetraphenylsiloles that are non-emissive in solution due to vibrational relaxation. It is already known that this concept can be extended to similar phosphole oxides.<sup>16</sup> To gain deeper insight into the nature of the fluorescence of these promising light-emitting materials, Yamaguchi *et al.* synthesized various 1-aryl-2,3,4,5-tetraphenylphosphole oxides (aryl = mesityl, 2,4,6-triisopropylphenyl, *p*-anilyl, 4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>) and investigated their emission behavior in the crystalline state.<sup>17</sup> The observed enhanced fluorescence with quantum yields of up to 91% is highly dependent on their packing motifs. Tang and coworkers used this concept to provide a showcase example for molecular engineering by using a benzophosphole oxide core (cf. Fig. 4) as a rigid central stator and attached flexible peripheral phenyl rotors.<sup>18</sup> By these means, they found an optimal balance between structural rigidity and flexibility to suppress aggregation-insensitive intramolecular motions, which can still deplete the photonic energy.

As already mentioned for solvatochromic materials, dithienophospholes (**11a,b**) and also  $\pi$ -extended derivatives thereof (**12** and **13**; Fig. 5) have gained attention as chromic materials.<sup>19</sup> **11a**, for example, shows strong AIE due to the suppression of a non-emissive photoinduced electron transfer (PET) from the alkoxybenzene donor to the phospholium acceptor scaffold, and by restricting the rotation of the benzyl moiety in the solid state. Compound **11b**, however, is less emissive in the solid state, which results from a strong ICT from the phenyl substituents to the phospholium  $\pi$ -system in solution.<sup>19</sup>

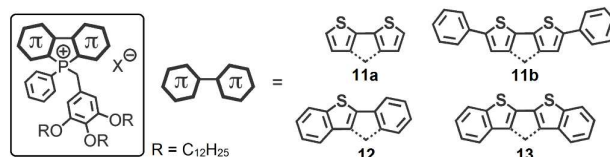


Fig. 5 A series of phospholes that show AIE, solvato-, mechano-, or thermo-chromism and that constitute the backbone of vapo- and halochromic materials.

It has already been demonstrated that phosphorus-based materials are an ideal platform to create, for example, suitable sensors for Lectin or explosive nitroaromatics.<sup>16</sup>

#### Mechanochromism. Stimulus: mechanical force

Putting chemicals under mechanical stress, e.g., by grinding, milling, or sonification, can also cause a color change, which is called mechanochromism. The reasons are manifold reaching from simple changes in the molecular geometries and phase transitions from one crystal structure to another, to distinct perturbations of the ground and excited states.<sup>1</sup> A phosphorus-containing compound that exhibits this kind of chromism after grinding (AG) of the solid is **11b** (Fig. 5).<sup>19</sup> The emission wavelength is shifted from 538 nm (yellow) to 560 nm (orange) and this process can be reversed upon thermal annealing (AT) at 80 °C multiple times without a measurable loss of response (Fig. 6). On the basis of detailed NMR

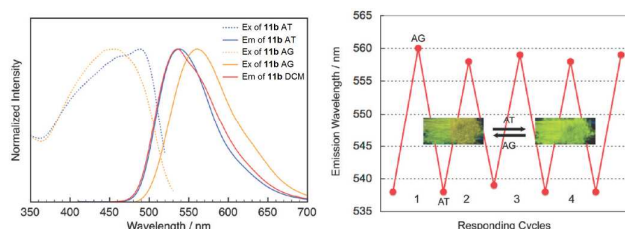


Fig. 6 Mechanochromism of **11b** (AT = after thermal annealing; AG = after grinding). Reprinted with permission from Ref 18. Copyright (2011) American Chemical Society.

spectroscopic and photophysical studies, this feature can be attributed to cooperative intermolecular interactions.<sup>19</sup> In a follow-up investigation, the response of the mechanically induced emission-signal change was amplified by a fluorescence resonance energy transfer (FRET) from the blue-emissive phosphole-lipid **11b** (donor) to an orange-emissive thienyl-substituted phosphole-lipid (acceptor).<sup>20</sup> As a result, a dropcast film of a 100:1 mixture of these two phospholium salts exhibited the typical blue emission of **11a** and is switched

to orange upon grinding.<sup>19</sup> A decreased intermolecular donor-acceptor separation distance  $r$  is responsible for this phenomenon because the FRET efficiency is proportional to  $r^{-6}$  due to the underlying dipole-dipole coupling mechanism.

These mechanochromic materials may be used as security markers in inks and papers or pressure-sensitive paints for engineering and aerodynamic flight modelling.<sup>1</sup>

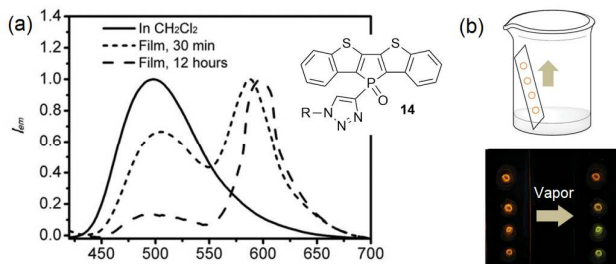
#### Thermochromism. Stimulus: temperature

Materials can undergo a color change caused by intrinsic or indirect thermochromism, i.e. whether the difference is a result from heat alone or from a difference in the environment around the chromophore brought about by heat, respectively.<sup>1</sup> The latter case can be found for all the phospholes **11–13** (Fig. 5).<sup>19</sup> Their emission spectra are varying strongly with temperature because of the flexible alkoxy chains that are attached to the photophysically active phospholium head group. Hypsochromic shifts of the emission wavelength maxima are observed at 213 K as opposed to the respective emission profiles at room temperature and are as large as 30 nm for the  $\pi$ -extended compound **12**.<sup>19</sup>

The main use of thermochromic materials is in paints or textiles.

#### Vapochromism. Stimulus: organic solvent vapor

Vapochromic systems are those that change color in response to a vapor of an organic compound or gas and typically adopt the original color upon changing the atmosphere, or heating. The reason for this change is the exposure to a different environment and thus closely related to that for solvatochromic materials.<sup>1</sup> Again, the dithienophosphole backbone of **13** shown in Fig. 5, has proven to be suitable to fashion this kind of chromism.<sup>21</sup> The aliphatic 3,4,5-tris(dodecyloxy)benzyl moiety was introduced via click chemistry and **14** thus features a 1,2,3-triazole spacer (Fig. 7). The resulting organogel is characterized by highly ordered self-assembled structures with an intense orange fluorescence both in solution and the solid state. In combination with an acceptor molecule such as green-fluorescent Rhodamine B, **14** can serve as a FRET donor, as already discussed for mechanochromic **11b** (Fig. 6). FRET, however, does not occur in solution, but is sensitive enough to be visible in the solid state when solvent residues are present. Thus, a carefully dried solid



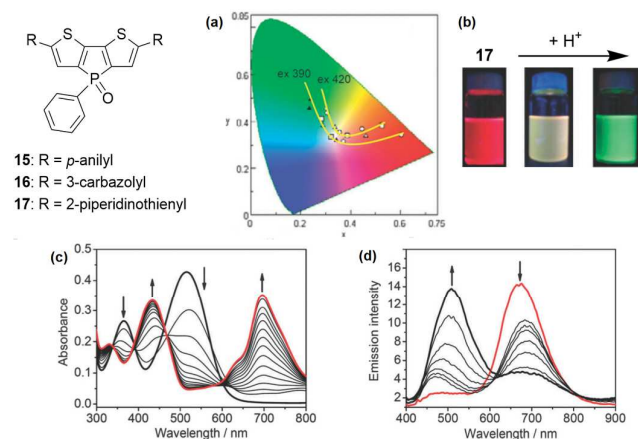
**Fig. 7** a) Emission spectra of a **14**:Rhodamine B mixture (100:1) in  $CH_2Cl_2$  solution (solid line) and the solid state (dotted, dashed lines after 30 min and 12 h of careful drying, respectively). b) Experimental setting (top) and fluorescent vapochromism (bottom). R = 3,4,5-tris(dodecyloxy)benzyl. Adapted with permission from Ref 20. Copyright (2014) John Wiley and Sons.

100:1 mixture of **14** and Rhodamine B changes its fluorescence from orange to green if exposed to volatile organic compounds (VOCs) such as  $CH_2Cl_2$ ,  $CHCl_3$ ,  $Et_2O$ , acetone, or MeOH. Even though selectivity is lacking, this material is still potentially useful in “electronic nose” devices for general air quality testing to indicate the presence of VOCs, which is one of the typical applications for vapochromic materials.<sup>21</sup>

#### Halochromism. Stimulus: pH

Halochromism is the occurrence of a color change induced by a pH-alteration and is a subclass of the more general phenomenon of ionochromism. The latter describes a color change of a compound upon interaction with an ionic species.<sup>1</sup> Here, the electron-accepting dithienophosphole core is utilized as key structural motif for this type of chromism by extension with  $p$ -anilyl donor moieties that can be protonated by trifluoroacetic acid (TFA; **15**; Fig. 8).<sup>21</sup> By exchanging the  $p$ -anilyl for a 3-carbazolyl donor, and setting up various donor-acceptor dyads, triads (e.g. **16**; Fig. 8), as well as polymeric structures, our group has expanded the scope of these halochromic materials significantly.<sup>23</sup> Furthermore, we were able to show that the color change-inducing protonation does not necessarily have to take place at the amine substituent but rather on the phosphoryl group of **16** that is better described as a  $P^+-O^-$  moiety.<sup>23</sup> In a follow-up study, 5-piperidinothienyl was introduced as donor substituent that can be protonated with TFA (**17**; Fig. 8).<sup>24</sup> This compound has so far the largest difference both in its absorption as well as in its emission spectrum upon protonation and changes its emission color from deep red ( $\lambda_{em} = 647$  nm) to green ( $\lambda_{em} = 510$  nm) in the presence of TFA. By fine-tuning both the excitation wavelength and the protonation equilibrium in  $CH_2Cl_2$  solution, white-light emission can efficiently be achieved from **17** and switched to green or red upon changing the pH (Fig. 8).<sup>24</sup>

Halochromic materials are predominant in analytical chemistry and best known as pH-sensitive dyes. In addition to that, these



**Fig. 8** Halochromic dithienophospholes **15–17**. (a) Commission Internationale de l'Éclairage (CIE) diagrams of **17** upon addition of TFA in  $CH_2Cl_2$  solution at different excitation wavelengths. (b) Photographs of the emission colors at different pH values. (c) Changes in the UV-Vis absorption and (d) emission spectra of **17** upon addition of TFA.<sup>23</sup>

compounds can be used as humidity indicators if combined with pH modifiers such as carboxylic acids.<sup>1</sup>

## Outlook

To date, organophosphorus and especially phosphole-based systems have been established to cover the commercially most valuable forms of chromism (electro-, photo-, solvato-, thermo-, and halochromism) and extend to the growing fields of AIE, mechano-, and vapochromism. However, only scattered reports of proof-of-concept devices for some of the mentioned chromic materials can be found in the literature. We hope that this Frontier article has provided the necessary stimulus for the next crucial step in the advancement of this field – a more vigorous translation of the gathered knowledge of potential applicability into practical applications.

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## ARTICLE

Journal Name

- 22 C. Romero-Nieto, S. Durben, I. M. Kormos and T. Baumgartner, *Adv. Funct. Mater.*, 2009, **19**, 3625-3631.
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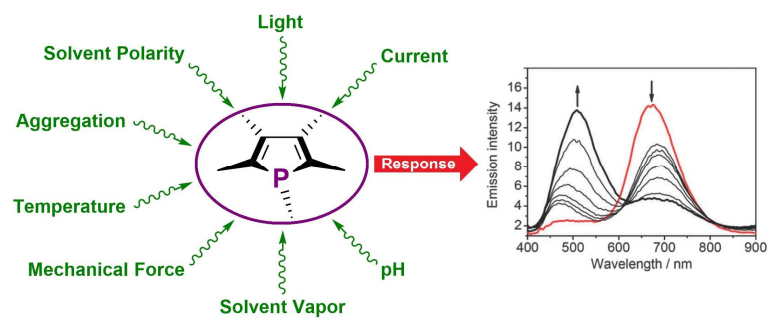
*Christian Reus, born in 1986, obtained his B.Sc. and M.Sc. degrees from Goethe University Frankfurt, Germany. In Matthias Wagner's research group he then investigated 9,10-dihydro-9,10-diboraanthracenes as efficient luminophores and received his PhD degree in 2014. Subsequently, he moved as a postdoctoral fellow to the University of Calgary, Canada, to work with Thomas Baumgartner in the field of organophosphorus chemistry. His research is focused on the design of electroactive small molecules and oligo-/polymers that are suitable as electrode materials for organic electrochemical storage devices. His PhD was supported by a scholarship from the Beilstein Foundation and he is currently the recipient of postdoctoral scholarships from the Alexander von Humboldt Foundation (Feodor Lynen scholarship) and the Killam Trusts.*

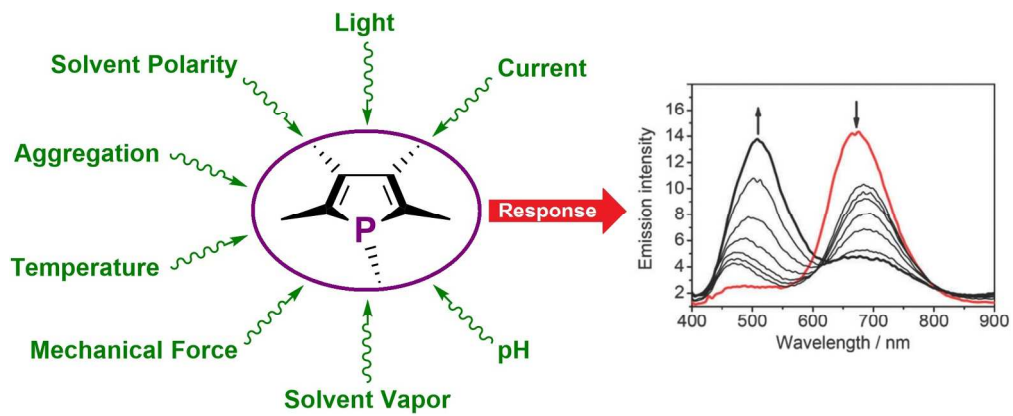


*Thomas Baumgartner received his PhD degree in 1998 from the University of Bonn, Germany, working with Edgar Niecke. From 1999 to 2002 he was a postdoctoral fellow at the University of Toronto, Canada, with Ian Manners. He started his independent career at the Johannes Gutenberg-University in Mainz (2002–2003) and at the RWTH-Aachen University (2003–2006), both in Germany. In 2006 he joined the Department of Chemistry at the University of Calgary, Canada, where he is Full Professor. His research interests are organophosphorus  $\pi$ -conjugated materials for sustainable energy applications. He has been recognized internationally with several awards including a Liebig fellowship from the German chemical industry association, an Alberta Ingenuity New Faculty Award, a JSPS invitation fellowship, and a Friedrich Wilhelm Bessel Research Award from the Alexander von Humboldt Foundation.*



The last five years have seen a huge advance in organophosphorus chemistry with respect to compounds with strong chromic responses to external stimuli. This Frontier article briefly summarizes these trends in order to highlight the broad versatility of especially phosphole-based scaffolds as chromic materials.





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