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Synthesis and Photophysical Properties of Donor–Acceptor Dithienophospholes

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The synthesis and detailed photophysical studies of a series of 2,6-asymmetrically functionalized dithieno[3,2-b:2',3'd]phospholes are reported. One-photon spectroscopy revealed that the materials show similar significant Stokes shifts supporting very polar excited intramolecular chargetransfer (ICT) states. Investigation of their two-photon absorption (TPA) behavior indicated that the materials are also

Introduction

Two-photon absorption (TPA) is a third-order nonlinear optical (NLO) process that has received a great deal of attention in the last decades due to its potential for practical application in two-photon fluorescence microscopy,^[1–3] 3D optical data storage and fabrication,^[4-8] optical limiting,^[9-11] photodynamic therapy,^[12-14] and multiphoton microscopy (MPM).^[15,16] Significant progress has been made with regard to the fine-tuning of fundamental photophysical parameters of organic TPA chromophores, such as nonlinear absorptivity range, TPA cross-section (σ_2), and fluorescence quantum yields ($\phi_{\rm PI}$), among other specific application requirements.^[17] In MPM applications, for example, most of the common practical fluorescent dyes have twophoton brightness values ($\sigma_2 \phi_{PL}$) in the range 1–300 GM^[18] with TPA excitation wavelengths in the biologically transparent range (800-1100 nm) that permit deeper penetration of biological tissues. To improve the TPA cross-section values, a variety of structural motifs has been investigated, both experimentally and theoretically, therefore allowing comprehensive TPA structure-property relationships.^[17,19] 2D molecules including dipolar (D- π -A) and quadrupolar (A- π -A, D- π -D), as well as 3D ones (octupolar and dendrimers) have been reported to show excellent TPA results.^[17]

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valuable TPA chromophores with reasonable cross-sections between 285–385 GM in the biologically relevant wavelength range 800–1100 nm. Moreover, the nonlinear optical features of the phosphole derivatives reported herein were found to remain almost unaltered after modification of the phosphorus center, either by oxidation and/or complexation.

In general, it has been concluded that the conjugation length, geometry, intramolecular charge transfer (ICT), polarizability, coplanarity, and the nature of the aromatic/ π bridge have a significant impact on TPA cross-sections.^[16,17] Moreover, 3D branching was also found, in some cases, to give rise to an enhancement in the TPA cross-section through cooperative effects.^[20] To date, a significant number of heterocycles have been employed in corresponding materials used as either an aromatic/ π -bridge or a donor-acceptor component.^[17] The phosphole system, a five-membered heterocycle, however, has received little attention in this context. This phosphorus-containing moiety presents some particularly intriguing characteristics that make it significantly different from other five-membered heterocycle analogues. The pyramidal disposition of the phosphorus center avoids efficient interaction between its lone pair orbital with the dienic, conjugated π system, reducing the aromaticity of the ring. Furthermore, this system also exhibits some $\sigma^* - \pi^*$ hyperconjugation through interaction of the exocyclic P–R bond with the π -conjugated system that lowers the LUMO energy level substantially. As a consequence, the electronic structure of phospholes can be readilv controlled by simple chemical modifications at the phosphorus center and/or at the main scaffold.^[21,22] In the late 1990s, theoretical studies already suggested that phospholes could indeed be useful building blocks for the engineering of dipolar chromophores with NLO properties.^[23] In 2002, Réau and co-workers determined the molecular first-hyperpolarizability values of phosphole derivatives for the first time. It was found that palladium-bridged dipolar phosphole dimers exhibit fairly high NLO activities assisted by the metal atom, which also preclude the phosphorus atom from further functionalization.^[24] Later on, Matano and co-workers^[25] described a series of new donor-acceptor 2aryl-5-styrylphosphole derivatives. These noncoordinated

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compounds showed higher first-hyperpolarizability values, demonstrating an effective inductive effect between the donor and acceptor moieties promoted by the vinylene bridge. Despite the promising results obtained in second-order nonlinear properties, some of us only very recently reported TPA cross-sections of dibenzophospholes, which turned out to be enhanced by spiro conjugation.^[26] Yamaguchi and coworkers reported earlier this year zwitterionic phosphonium-borate containing ladder-type acenes with very large TPA cross-sections of up to 784 GM when excited at 1200 nm.^[27]

A few years ago, we introduced the dithieno [3,2-b:2',3'-d]phosphole as a novel phosphorus-based building block,^[28] which has successfully been employed in a variety of materials, ranging from oligomers to polymers and dendrimers with excellent optical properties.^[28-30] The unique structural and photophysical properties of this distinct type of phosphole, such as its versatile reactivity, tunability, and intense fluorescence with high quantum yields, make it particularly attractive in the conception of new and improved materials. The ideal materials design for NLO applications requires the structure and, more importantly, the photophysical properties of TPA chromophores to be adaptable to a specific function. From this viewpoint, we decided to evaluate the TPA capabilities of donor-acceptor dithienophosphole model compounds and to successively investigate the influence of the oxidation state of the phosphorus atom and/or the variation of the third structural dimension on its TPA properties. In this report we now describe the synthesis and characterization of novel donor-acceptor vinylene-bridged dithieno[3,2-b:2',3'-d]phospholes, as well as a comprehensive investigation of their one-photon and two-photon absorption features.

Results and Discussion

Synthesis and Characterization

For the purpose of this study, three donor-acceptor dithienophosphole derivatives were synthesized according to Scheme 1. The general synthetic strategy towards these systems involved a stepwise Wittig-Horner coupling protocol between aldehyde 1^[29e] and *para*-substituted donor or acceptor benzylphosphonates. In a recent study on symmetrically substituted dithienophospholes, we could verify that this coupling leads to selective formation of E-configured vinylene bridges.^[29e] In variation to our published procedure, building block 1 was treated with diethyl 4-(diphenylamino)benzylphosphonate (1.3 equiv.), vielding monofunctionalized compound 2 in 74% yield. Access to this monosubstituted compound benefits from our observations that the Wittig-Horner coupling only proceeds very slowly when electron-donating benzyl moieties are used. From this asymmetric compound, a second Wittig-Horner reaction with diethyl 4-(trifluoromethyl)benzylphosphonate gave rise to 3 in 93% yield, which showed a ${}^{31}P{}^{1}H$ NMR signal at $\delta = -19.9$ ppm. Importantly, this synthetic protocol allowed us to preserve the trivalent phosphorus

throughout the whole reaction sequence. The expected ${}^{3}J_{\rm H H}$ coupling constants of 16.0 (±0.1) Hz for the vinylic protons in the ¹H NMR spectrum clearly supported the selective formation of E-configured double bonds. To determine the influence of the phosphorus oxidation state on the potential TPA properties of the system, compound 3 was then oxidized in a standard procedure involving H₂O₂.^[28] The ³¹P{¹H} NMR signal at $\delta = 18.1$ ppm supported the successful oxidation of the phosphole moiety. Furthermore, we were also interested in attaching a bulky group at the phosphorus center to insert an out-of-plane moiety (apart from the intrinsic phenyl ring) to modify the third spatial dimension of the molecule. As mentioned above, it has been demonstrated that 3D branched molecules can potentially lead to synergistic effects by through-space interactions enhancing the TPA features.^[17] The intriguing optoelectronic properties demonstrated by dithienophosphole gold complexes in general,^[30] encouraged us to use the gold(I) chloride fragment as an out-of-plane unit. Treatment of 3 with Au(THT)Cl (THT = tetrahydrothiophene) at room temperature provided the corresponding donor-acceptor phosphole gold complex 5 in excellent yield (96%); the characteristic ³¹P{¹H} NMR signal at δ = 8.9 ppm confirmed its successful formation.^[30] All new compounds were fully characterized by heteronuclear NMR spectroscopy (¹H, ¹³C, ³¹P), mass spectrometry, and elemental analysis. Complete data are provided in the Experimental Section.



Scheme 1. Synthesis of donor–acceptor dithieno[3,2-*b*:2',3'-*d*]phosphole derivatives.

Linear (One-Photon) Absorption and Emission Spectroscopy

To gain detailed information on the excited states of the new donor-acceptor dithienophospholes and to acquire deeper insight into important structure-property relationships, we first studied the one-photon absorption (OPA) features of the different derivatives. Importantly, all compounds are transparent to linear absorption between 800 and 1100 nm, preventing possible residual absorptions during the TPA measurements. The single-photon photophysical properties of compounds 2–5 in dichloromethane (DCM) and 2-methoxyethanol (ME) are listed in Table 1 (see also Figure 1).

Table 1. One-photon photophysical properties.

	Solvent ^[a]	$\lambda_{\rm abs}$	λ _{em}	log ɛ[c]	$\Delta v^{[d]}$	η ^[e]	$\phi_{\rm PL}^{\rm [f]}$
		[nm]	[nm]		$[cm^{-1}]$	[ns]	[%]
2	DCM	453, 503 ^[b]	633	nd	nd	nd	24
3	DCM	474	631	nd	5249	$\begin{array}{c} 1.08 \pm 0.005 \\ (52.1\%) \\ 2.48 \pm 0.004 \\ (47.9\%) \end{array}$	25
	ME	491	643	5.15	4814	nd	15
4	DCM	489	628	nd	4526	$\begin{array}{c} 0.94 \pm 0.007 \\ (33.2\%) \\ 2.43 \pm 0.003 \\ (66.8\%) \end{array}$	24
	ME	492	645	5.14	4821	nd	12
5	DCM	479	627	nd	4928	$\begin{array}{c} 0.55 \pm 0.003 \\ (76.4\%) \\ 1.32 \pm 0.016 \\ (21.8\%) \\ 4.01 \pm 0.035 \\ (1.8\%) \end{array}$	14
	ME	484	638	5.29	4987	nd	10

[a] DCM = CH₂Cl₂; ME = 2-methoxyethanol. [b] λ_{max} excitation. [c] Molar extinction coefficient. [d] Stokes shift ($\Delta v = 1/\lambda_{abs} - 1/\lambda_{em}$). [e] Fluorescence lifetime; decay curves were analyzed with two or three exponential components. The number in brackets is the amplitude ratio in %. [f] Fluorescence quantum yield relative to fluorescein (in 0.01 M KOH/ethanol); $\pm 15\%$. nd = not determined.



Figure 1. Normalized absorption and emission of compounds 3, 4, and 5 in DCM.

The absorption maxima of all compounds are in the range $\lambda_{\text{max}} = 484-492$ nm in ME and $\lambda_{\text{max}} = 474-489$ nm in DCM. These results are quite remarkable since it has commonly been observed that oxidation of the phosphorus atom is accompanied by a redshift (<40 nm) in the absorption and emission spectra.^[28] The same is true for transition-metal-complexed phospholes, which undergo a less pronounced bathochromic shift (<20 nm)^[28,30] compared to noncoordinated dithienophospholes. In this case, the

very slight changes in the absorption spectra reveal that the oxidation and complexation of the phosphorus atom located at the center of the π -conjugated molecules have almost no effect on the linear absorption properties of the system. The absorption maxima of compounds 3-5 were, however, found to be redshifted with the solvent polarity upon moving from DCM to ME. This positive solvatochromism effect indicates that the electronic state reached after excitation is more polar than the ground state.^[31] With respect to the fluorescence features, similar deep-red emission maxima were observed for compounds 3-5 in solution (DCM: $\lambda_{em} = 627-631$ nm, ME: $\lambda_{em} = 638-645$ nm). Again, the emission properties remained almost unaltered after either oxidation or complexation of the central phosphole moiety. Notably, these emissions represent the most redshifted values in term of wavelengths by using phosphole oligomers to date, and illustrate the high value of the donor-acceptor approach to lowering optical band gaps. Moreover, the observed Stokes shifts of $\Delta v = 4526$ -5249 cm⁻¹ (DCM) and $\Delta v = 4814-4987$ cm⁻¹ (ME) are rather large for dithienophospholes,^[28] which is a clear indication of the high polarizability of the π -conjugated system. Furthermore, it is well established that donor-acceptorfunctionalized molecules can lead to intramolecular charge transfer (ICT) processes, which would explain the large Stokes shifts observed. Typical ICT consists of the charge redistribution from the donor to acceptor unit upon excitation. As a result, the global charge of the molecule undergoes a rearrangement that gives rise to charge-separated excited states. Fluorescence lifetime decay measurements also pointed to such a process. Experimental values are summarized in Table 1. In line with the observed Stokes shifts, the multiexponential fit of the fluorescence decay is a further indication that complex relaxation mechanisms of the locally excited state toward the ground state are taking place.^[32] In addition, to support a possible ICT, DFT calculations were performed for compounds 3 and 4 at the B3LYP/6-31G* level of theory. The optimized structures possess a high degree of coplanarity, which is a beneficial factor for the communication between the donor and acceptor end groups, hence favoring NLO phenomena in general. The calculated frontier orbitals for compound 3 are shown in Figure 2 (see Supporting Information for 4). The HOMO is largely located at the donor end of the materials, whereas the LUMO is located at the acceptor end, demonstrating an efficient conjugation along the extended conjugated backbone.

Despite the differences between the absorption and emission values, the quantum yields (ϕ_{PL}) for compounds **3**, **4**, and **5** in DCM are relatively high at $\phi_{PL} = 25$, 24, and 14%, respectively. The oxidation of the phosphorus atom does not seem to affect the fluorescence quantum yields. However, the ϕ_{PL} value of the gold complex is slightly lower, probably due to the heavy atom effect. Donor–acceptor structural motifs, in general, lead to a decrease in the ϕ_{PL} values.^[33] Intriguingly, the donor–acceptor phosphole derivatives only show a minor decrease when compared with their quadrupolar homologues,^[29e] which makes these de-



Figure 2. Frontier orbitals of compound **3**. Top: LUMO; bottom: HOMO; (B3LYP/6-31G* level of theory).

rivatives particularly interesting for the study of TPA-induced fluorescent applications. Because of the magnitude of the observed Stokes shifts, we wanted to discern other possible phenomena besides ICT that could interfere with the TPA measurements. Particularly, undesired aggregations in the excited state could also contribute to the crosssection values^[34] and thus to inaccurate structure-property relationships. To eliminate this possibility, concentration experiments were carried out for compounds 3-5 and a similar trend was observed for all of them. We recorded their absorption and emission spectra with increasing the concentration from 10⁻⁷ to 10⁻⁵ M in ME (see Supporting Information). However, even after these two orders of magnitude increments, no changes either in the absorption or in the emission maxima could be detected. Therefore, concentration dependent aggregation could be discarded from these experiments.

Due to the very similar photophysical features of compounds 3–5, we representatively chose compound 4 to carry out more detailed one-photon investigations. To examine the solvatochromism of compound 4, the absorption and emission spectra were recorded in a variety of different solvents (see Table 2).

Although some minor deviation from the trend was detected in the absorption features when increasing the solvent polarity [according to the Et(30) scale], a strong solvatochromism effect can be observed for the emission features. The shortest emission wavelength maximum at $\lambda_{em} =$ 591 nm in the least polar solvent (toluene) is redshifted by about $\Delta \lambda_{em} = 54$ nm upon using ME as solvent ($\lambda_{em} =$ 645 nm). Thus, the solvent polarity allows significant tuning of the luminescence properties of the material. It is noteworthy that the range of the emission maxima (591– 645 nm, $\Delta \lambda_{em} = 54$ nm) is five times larger than the range of the absorption maxima (481–492 nm, $\Delta \lambda_{abs} = 11$ nm) on

Table 2. Photophysical properties of compound **4** in different solvents.

Solvent	Polarity Et(30)	$\lambda_{\rm abs} [{\rm nm}]$	$\lambda_{\rm em} [{\rm nm}]$	$\Delta v \ [\mathrm{cm}^{-1}]^{[\mathrm{a}]}$	$\phi_{\rm PL} \ [\%]^{[b]}$
Toluene	33.9	486	591	3656	20
Ether	34.5	481	592	3870	20
THF	37.4	485	607	4144	22
AcOEt	38.1	483	608	4257	21
CHCl ₃	39.1	492	619	4170	24
DCM	40.7	489	628	4526	24
DMF	43.2	489	640	4825	14
EtOH	51.9	489	641	4849	12
ME	52.0	492	645	4821	12

[a] Stokes shift ($\Delta v = 1/\lambda_{abs} - 1/\lambda_{em}$). [b] Fluorescence quantum yield relative to fluorescein (in 0.01 M KOH/ethanol); $\pm 15\%$.

increasing the polarity of the medium (see Table 2). Such characteristic behavior, as well as the large Stokes shifts, even in non-polar solvents, reveal that a significant degree of electronic reorganization takes place upon excitation and this gives rise to a polar charge-separated emitting state, as anticipated previously. This feature is also supported by the large excited state dipole moment of $\mu_e = 34.2 \text{ D}$ for 4 that was estimated by the Lippert-Mataga model^[35] on the basis of the solvatochromism and the DFT-computed groundstate dipole moment of $\mu_g = 8.6$ D. As a consequence of the interaction between the dipole moments of the compound and the solvent molecules, the fluorescence quantum yields are significantly influenced by the solvent polarity, from $\phi_{\rm PL}$ = 20% (toluene) to ϕ_{PL} = 12% (EtOH, ME). Finally, it is important to note that compounds 3-5 exhibit high photostability during the performed experiments; no decomposition or *cis/trans* isomerization processes were detected.

Nonlinear (Two-Photon) Absorption Spectroscopy

TPA spectra of compounds 3-5 in DCM and ME are shown in Figure 3. All three compounds show a very broad absorption along the whole range employed in biological applications ($\Delta \lambda_{2max} = 800-1100 \text{ nm}$). Almost no differences were found between the spectra recorded in DCM and ME, suggesting that the two-photon excited states are hardly affected by the polarity of the medium. The maximum cross-section values are listed in Table 3. All compounds present moderately high cross-sections around σ_2 = 335–385 GM in DCM and $\sigma_2 = 285-345$ GM in ME that are larger than those of somewhat related donor-acceptor and donor-donor dithienothiophene analogues.[36] According to the double level model,^[17] donor-acceptor molecules usually present TPA maxima in around double the wavelength of the single-photon absorption peak. However, no clear TPA maxima were detected around twice the OPA maxima for all compounds, although a very small peak is located there. Despite a triple level model being potentially applicable, the explanation for this deviation is currently unclear, but, however, is under detailed investigation. Similar to the single-photon absorption studies, TPA properties of the materials remained almost unchanged when varying the oxidation state of the phosphorus center from +3 to +5. Recently, it has been demonstrated in pure metal complex TPA chromophores that a change in the oxidation state of the metal center can lead to dramatic changes in their nonlinear responses.^[37] Interestingly however, the third-order response of the donor-acceptor dithienophosphole derivatives appears to be preserved after chemical/structural modifications at the phosphorus center. By complexation of the phosphorus atom, we evaluated whether the TPA properties could also be impacted through interactions between the out-of-plane orbitals of the Au-Cl fragment and the phosphole main scaffold. However, although the cross-section was indeed slightly increased, the interactions were not significant enough to claim major changes in the TPA properties. Compared to the notable enhancement in secondorder NLO properties by complexation of related phospholes,^[24] it can be concluded that the TPA properties of donor-acceptor dithienophospholes are relatively silent toward complexation of the phosphole center. This fact, together with the preservation of the TPA features in the different oxidation states of the phosphorus center (+3, +5), are particularly interesting since they offer the possibility of (1) obtaining dithienophospholes with specific cross-sections and, consecutively, (2) taking advantage of the versa-



Figure 3. TPA spectra of compounds 3 (top), 4 (middle), and 5 (bottom) in DCM and in ME.



tile reactivity of the phosphorus atom to be structurally/ chemically adapted to precise applications while keeping the TPA features intact.

Table 3. TPA properties of compounds 3-5.

Compound	Solvent	$\lambda_{\rm max} [\rm nm]^{[a]}$	σ ₂ [GM] ^[b]
3	DCM	817	335
	ME	819	285
4	DCM	817	385
	ME	819	320
5	DCM	817	375
	ME	819	345

[a] TPA wavelength maxima. [b] TPA cross-section: $GM = 10^{-50} \text{ cm}^4 \text{ s photon}^{-1}$.

Conclusions

In summary, a new series of 2,6-donor-acceptor-functionalized dithienophosphole derivatives has been synthesized that can structurally be modified by simple and efficient reactions at the phosphorus center. Their linear and nonlinear optical properties have been studied. Investigation of their photophysical properties revealed large Stokes shifts with significant fluorescence quantum yields and high photostability. For the first time, two-photon absorption properties of asymmetric donor-acceptor dithieno[3,2b:2',3'-d phosphole derivatives have been reported. All compounds show moderately high TPA cross-sections in the wavelength range suitable for biological/biomedical applications. Furthermore, the third-order nonlinear optical properties were found to remain unaltered after structural/ chemical modifications at the phosphole center, which opens the possibility to develop TPA chromophores that can easily and efficiently be modified a posteriori for specific applications. Currently, we aim to explore suitable donoracceptor dithienophosphole derivatives as selective molecular biomarkers for imaging applications.

Experimental Section

General Procedures and Spectroscopic Measurements: All manipulations were carried out under a dry nitrogen atmosphere by employing standard Schlenk techniques. Column chromatography was carried out by using silica gel (70-230 mesh, 60 Å) and aluminum oxide (activated, neutral, Brockmann I, standard grade, ≈150 mesh, 58 Å). Solvents were dried by using standard procedures. H_2O_2 and tBuOK were purchased from Aldrich and used as received. 2,6-Diformyldithieno[3,2-b:2',3'-d]phosphole (1),[29e] diethyl 4-(trifluoromethyl)benzylphosphonate,[38a] diethyl 4-(diphenylamino)benzylphosphonate,^[38b] and Au[THT]Cl^[38c] were prepared according to literature procedures. ³¹P{¹H} NMR, ¹H NMR, and ¹³C{H} NMR spectra were recorded with a Bruker DMX-300 or Bruker DRX-400 spectrometer. Chemical shifts were referenced to external 85% H₃PO₄ (³¹P) and external TMS (¹³C, ¹H). Electron ionization (70 eV) mass spectra were obtained with a Finnigan SSQ 7000 spectrometer, and electrospray ionization mass spectra were obtained with a Bruker Daltonic Esquire 3000 spectrometer. All fluorescence experiments were recorded by using HPLC-grade solvents

with a Jasco FP-6600 spectrofluorometer and UV/Vis/NIR Cary 5000 spectrophotometer. The fluorescence decay was measured by the time-correlated single-photon counting (TCSPC) method under air-saturated conditions.

TPA Measurements: TPA spectra were measured by an open-aperture Z-scan method with an optical parametric amplifier (pulse width typ. 140 fs, 1.0 kHz repetition rate, incident power = 0.05-0.4 mW varying at least four different powers for each measurement point). The incident power approximately corresponds to the on-axis peak intensity I_0 of 200 GW/cm² or less at the focal point. The Rayleigh range of the setup was typically 4-6 mm depending on the wavelength. The sample solution (1.3-2.7 mM) was held in a 1-mm quartz cuvette. The details of the setup were reported elsewhere.^[39] The recorded open-aperture Z-scan traces (see Supporting Information for typical traces) were analyzed by curve fitting with a model function assuming the energy transmittance of a temporal and spatial Gaussian pulse through a two-photon absorptive media.^[20b] The TPA coefficient β was obtained from the linear plot of the two-photon absorbance, q_0 . The latter was obtained from the curve fitting against the incident power because q_0 is linear to I_0 (therefore, to the incident power) for TPA. TPA cross-section σ_2 was obtained from the convention $\sigma_2 = \beta \lambda / (hcN)$, where N is the number density of the molecule, λ is the incident wavelength, c is the speed of light, and h is the Planck's constant.

Compound 2: tBuOK (147 mg, 1.3 mmol, 1.2 equiv.) was added in small portions to a solution of 1 (360 mg, 1.1 mmol, 1 equiv.) and diethyl 4-(diphenylamino)benzylphosphonate (563 mg, 1.4 mmol) in THF (50 mL) at -78 °C. After 1 h, the reaction mixture was allowed to reach room temperature and stirred for an additional 4 h. H₂O was added, and the crude was neutralized with HCl (2 M). The product was extracted with CH₂Cl₂, and the organic layer was dried with MgSO₄. After evaporation of the solvent, the crude was purified by column chromatography (SiO₂, DCM as eluent) to obtain a red solid (463 mg, 74%). ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 9.85 (s, 1 H, CHO), 7.79 (s, 1 H, thiophene), 7.37–7.25 (m, 10 H), 7.13–7.01 (m, 11 H), 6.92 (d, ${}^{3}J_{H,H} = 15.9$ Hz, 1 H, -CH=CH-) ppm. ¹³C NMR (101 MHz, CDCl₃, 25 °C): δ = 182.7 (s, CHO), 148.2 (s, Ar), 147.5 (s, Ar), 147.4 (d, J_{C,P} = 5.4 Hz, thiophene), 141.1 (s, thiophene), 136.4 (s, thiophene), 132.9 (d, ${}^{2}J_{C,P}$ = 21.21 Hz, o-Ph), 130.2 (s, ArH), 129.9 (s, ArH), 129.6 (s, p-Ph), 129.6 (s, ArH), 129.2 (d, ${}^{3}J_{C,P}$ = 8.1 Hz, *m*-Ph), 127.9 (s, ArH), 127.7 (s, ArH), 125.0 (s, ArH), 125.0 (s, ArH), 123.6 (s, ArH), 122.9 (s, ArH), 119.8 (s, ArH) ppm. ³¹P{¹H} NMR (162 MHz, CDCl₃, 25 °C): δ = -20.0 ppm. C₃₅H₂₄NOPS₂ (569.68): calcd. C 73.79, H 4.25, N 2.46; found C 73.58, H 4.58, N 2.42.

Compound 3: To a mixture of compound 2 (180 mg, 0.3 mmol) and 4-(trifluoromethyl)benzylphosphonate (121 mg, 0.41 mmol. 1.3 equiv.) was added tBuOK (43 mg, 0.4 mmol, 1.2 equiv.) at -78 °C. The reaction mixture was stirred for 1 h at low temperature and allowed to reach room temperature. After 4 h, H₂O was added, and the crude was neutralized with 2 M HCl. The product was extracted with CH₂Cl₂, and the organic layer was dried with MgSO₄. After evaporation of the solvent, the crude was washed with heptane to obtain an orange solid (198 mg, 93%). ¹H NMR (300 MHz, $[D_6]$ acetone, 25 °C): δ = 7.80–7.68 (m, 6 H), 7.62–7.58 (m, 1 H), 7.50-7.19 (m, 13 H), 7.15-6.96 (m, 9 H) ppm. ¹³C NMR (75 MHz, CD_2Cl_2 , 25 °C): δ = 148.5 (s, thiophene), 148.3 (s, thiophene), 148.2 (s, Ar), 148.0 (s, Ar), 146.1 (s, Ar), 141.1 (s, Ar), 140.9 (s, Ar), 132.9 (d, ${}^{2}J_{C,P}$ = 20.3 Hz, *m*-Ph), 128.4 (s, Ar), 127.7 (s, ArH), 126.9 (s, Ar), 126.1 (q, J_{C,F} = 2.7 Hz, Ar), 125.2 (s, ArH), 125.0 (s, ArH), 124.4 (s, ArH), 124.7 (q, J_{C,F} = 274.2 Hz, Ar), 123.8 (s, ArH), 123.6 (s, ArH), 120.6 (s, ArH) ppm. ³¹P{¹H} NMR (162 MHz, CDCl₃,

25 °C): δ = -19.9 ppm. MS (EI, 70 eV): m/z (%) = 711 (100) [M]⁺. C₄₃H₂₉F₃NPS₂ (711.80): calcd. C 72.56, H 4.11, N 1.97; found C 72.65, H 3.89, N 1.96.

Compound 4: Asymmetric compound 3 (80 mg, 0.1 mmol) was treated with hydrogen peroxide (0.5 mL, 33% w/v) in CH₂Cl₂ (25 mL) at room temperature overnight. After removing all volatiles under vacuum, the residue was taken up in CH₂Cl₂ again and then filtered over alumina. Evaporation of the solvent afforded a red solid (70 mg, 98%). ¹H NMR (400 MHz, CD_2Cl_2 , 25 °C): δ = 7.75 (dd, ${}^{3}J_{PH}$ = 13.6 Hz, J = 7.6 Hz, 2 H, o-Ph), 7.63–7.55 (m, 5 H), 6.90–6.95 (m, 1 H), 7.46 (td, J = 7.6 Hz, ${}^{4}J_{PH} = 3.2$ Hz, 2 H, *m*-Ph), 7.35–7.26 (m, 7 H), 7.17 (d, J = 2.8 Hz, 1 H), 7.11–7.05 (m, 8 H), 7.02-6.99 (m, 3 H) ppm. ¹³C NMR (75 MHz, CD₂Cl₂, 25 °C): δ = 149.1 (s, thiophene), 148.9 (s, thiophene), 148.5 (s, Ar), 147.9 (s, Ar), 146.6 (s, Ar), 140.6 (s, Ar), 140.4 (s, Ar), 139.7 (d, ${}^{1}J_{C,P}$ = 112.3 Hz, *ipso*-thiophene), 133.1 (d, $J_{C,F}$ = 2.8 Hz, Ar), 131.3 132.9 (d, ${}^{2}J_{C,P}$ = 11.3 Hz, thiophene), 130.5 (s, ArH), 130.1 (s, ArH), 129.9 (s, ArH), 129.5 (d, ${}^{2}J_{C,P}$ = 12.9 Hz, o-Ph), 128.1 (s, ArH), 127.9 (s, ArH), 127.1 (s, ArH), 126.1 (q, J_{C.F} = 3.6 Hz, Ar), 125.4 (s, ArH), 124.3 (q, $J_{C,F}$ = 270.75 Hz, Ar), 124.1 (s, ArH), 124.1 (s, ArH), 123.4 (s, ArH), 119.5 (s, ArH) ppm. ³¹P{¹H} NMR (162 MHz, CDCl₃, 25 °C): δ = 18.1 ppm. MS (EI, 70 eV): m/z (%) = 727 (98) $[M]^+$, 364 (100). $C_{43}H_{29}F_3NOPS_2$ (727.80): calcd. C 70.96, H 4.02, N 1.92; found C 70.63, H 4.37, N 1.73.

Compound 5: Asymmetric compound 3 (100 mg, 0.14 mmol) was treated with Au[THT]Cl (45 mg, 0.14 mmol) in CH₂Cl₂ (10 mL) at room temperature for 1 h. After removing all volatiles under vacuum, the residue was purified by washing with diethyl ether and pentane and then crystallized from DCM/pentane to afford a red solid (127 mg, 96%). ¹H NMR (400 MHz, CD₂Cl₂, 25 °C): δ = 7.75 (dd, ${}^{3}J_{\rm PH}$ = 14.8 Hz, J = 7.2 Hz, 2 H, o-Ph), 7.59–7.52 (m, 5 H), 7.46 (td, J = 8.0 Hz, ${}^{4}J_{P,H} = 2.8$ Hz, 2 H, *m*-Ph), 7.32–7.22 (m, 7 H), 7.09–6.89 (m, 13 H) ppm. ¹³C NMR (101 MHz, CDCl₃, 25 °C): $\delta = 148.6$ (d, $J_{C,P} = 13.8$ Hz, thiophene), 148.3 (d, $J_{C,P} = 13.9$ Hz, thiophene), 147.5 (s, Ar), 147.4 (s, Ar), 146.2 (s, Ar), 140.0 (s, Ar), 149.8 (s, Ar), 138.0 (d, ${}^{1}J_{C,P}$ = 67.67 Hz, *ipso*-thiophene), 133.7 (d, $J_{C,P}$ = 15.9 Hz, Ar), 133.1 (br. s, Ar), 131.1 (s, Ar), 130.1 (s, ArH), 129.8 (d, ${}^{2}J_{C,P}$ = 13.0 Hz, thiophene), 129.8 (s, ArH), 129.6 (s, ArH), 127.7 (s, ArH), 127.7 (s, ArH), 126.8 (s, ArH), 126.0 (br. s, Ar), 126.0 (d, J_{C,P} = 62.216 Hz, *ipso*-Ph), 125.1 (s, ArH), 125.0 (s, ArH), 124.5 (q, J_{CF} = 271.0 Hz, Ar), 118.9 (s, ArH) ppm. ³¹P{¹H} NMR (162 MHz, CDCl₃, 25 °C): δ = 8.9 ppm. MS (ESI+): m/z = 943 [M]⁺, 605 [M – PhPAuCl]⁺. C₄₃H₂₉AuClF₃NPS₂ (944.22): calcd. C 54.70, H 3.10, N 1.48; found C 55.01, H 2.89, N 1.36.

Supporting Information (see footnote on the first page of this article): Photophysical details on the concentration studies for 3–5; solvatochromism for 4; DFT calculations for 4; fluorescence decay measured by the time-correlated single-photon counting (TCSPC) method for compounds 3–5; details on TPA measurements for 3–5.

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