Effects of meso-M(PPh$_3$)$_2$Cl (M = Pd, Ni) substituents on the linear and third-order nonlinear optical properties of chalcogenopyrylium-terminated heptamethines in solution and solid states†‡

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Aggregation of cyanine-like dyes can significantly affect their optical properties. Here we report the effects of bulky meso-M(PPh$_3$)$_2$Cl (M = Pd, Ni) substitution on the molecular and solid-state optical characteristics of chalcogenopyrylium-terminated heptamethines. Metallated dyes were synthesised by reaction of the meso-chloro dyes with Pd(PPh$_3$)$_2$ or Ni(PPh$_3$)$_2$ at room temperature. The two PPh$_3$ ligands are trans and the plane formed by the metal atom and its ligands is approximately orthogonal to that of the polymethine π-system. Replacement of Cl by M(PPh$_3$)$_2$ leads to a large blue shift of the solution absorption maximum and a decrease in the associated transition dipole moment, these effects being slightly more pronounced for Ni than for Pd. DFT calculations and electrochemical data suggest the blue shifts can largely be attributed to destabilisation of the LUMO by the more strongly π-donating M(PPh$_3$)$_2$Cl groups. The magnitude of the real part of the molecular third-order polarisability, Re(γ), decreases in the order Cl > Pd(PPh$_3$)$_2$Cl ≫ Ni(PPh$_3$)$_2$Cl. Within the framework of the sum-over-states expression for Re(γ), the difference between Cl and Pd(PPh$_3$)$_2$Cl examples can be rationalised considering the effects of the $S_0 \rightarrow S_1$ transition energy and transition dipole moment on the two-state term associated with $S_0 \rightarrow S_1$. On the other hand, the magnitude of Re(γ) for a Ni(PPh$_3$)$_2$Cl dye is anomalously low; SAC-CI/CI/HF/cc-pVDZ excited-state calculations reveal this is due to a two-photon-allowed $S_2$ state at unusually low energy for a cyanine-like dye, leading to a large positive three-state contribution to $γ$ opposing the negative two-state $S_2$ term. Thus, despite a cyanine-like molecular structure and linear absorption spectrum, this compound does not exhibit cyanine-like nonlinear optical behavior. Turning to the effects on aggregation, molecular dynamics simulations suggest that Pd(PPh$_3$)$_2$Cl substitution largely suppresses H- and J-aggregate formation; indeed experimental absorption spectra for neat films of Pd(PPh$_3$)$_2$Cl-substituted dyes are fairly similar to corresponding solution spectra. A 50 wt% blend of a Pd(PPh$_3$)$_2$Cl-substituted telluropyrylium-terminated dye with amorphous polycarbonate exhibits a third-order susceptibility of $-3 \times 10^{-11}$ esu, a two-photon figure-of-merit in excess of 10, and linear loss of 6.3 dB cm$^{-1}$, which are close to the requirements for all-optical switching applications.

Introduction

Many cyanine-like polymethine dyes form aggregates in the solid state or in concentrated solid or liquid solutions, their very large polarisabilities lead to strong van der Waals attractions that can outweigh electrostatic repulsions between like-charged dyes. J-aggregates have long played an important sensitising role in the silver halide photographic process, while their strongly emissive properties have led to use in biological imaging and as probes of internanoparticle interactions. Broadening of absorption by the presence of...
H-like aggregates may be beneficial in light-harvesting applications.\textsuperscript{5} However, in other applications, dye–dye interactions can be detrimental. In particular, although the molecular-level properties of cyanine-like dyes are attractive for third-order nonlinear optical (NLO) applications, especially all-optical switching (AOS) applications that rely on the nonlinear refractive index, these properties can be dramatically modified by aggregation.\textsuperscript{6}

For AOS applications, (i) the real part of the third-order susceptibility, $\text{Re}(\chi^{(3)})$, at the wavelength of interest should be large in magnitude; (ii) nonlinear optical losses from two-photon absorption (2PA) should be small, i.e., the imaginary part of third-order susceptibility, $\text{Im}(\chi^{(3)})$, should be minimised; and (iii) linear optical losses from one-photon absorption (1PA) and/or scattering should be low.\textsuperscript{7–9}

Perturbation theory allows the complex frequency-dependent susceptibility to be expressed using a “sum-over-states” expression. The static (zero-frequency) real part of the third-order polarisability, $\text{Re}(\gamma_0)$, the molecular quantity corresponding to $\text{Re}(\chi^{(3)})$, is given by

$$\text{Re}(\gamma_0) \propto -\frac{(\mu_{ge}^4)}{(E_{ge}^3)} + \frac{(\mu_{ge}^2\Delta\mu_{ge}^2)}{(E_{ge}^5)} + \sum_{\epsilon} \frac{(\mu_{ge}^2\mu_{ee}^2)}{E_{ge}^2E_{ee}^2}$$

where $\mu$, $\Delta\mu$, and $E$ denote transition dipole moments, changes in state dipole moment, and transition energies, respectively, and subscripts $g$, $e$, and $\epsilon$ denote ground, first excited, and higher-lying excited states, respectively.\textsuperscript{10,11}

Typical cyanine-like polymethines generally exhibit large negative $\text{Re}(\gamma_0)$ due to a large negative “N” term, and relatively small positive “D” and “T” terms. The large “N”-term arises due to the strong (high-$\mu_{ge}$) low-energy (small $E_{ge}$) 1PA-allowed $S_0-S_1$ transition. Although such symmetrical cyanines have $C_{2v}$ symmetry, they are quasi-linear and, thus, almost centro-symmetric; accordingly $\Delta\mu_{ge}$, and consequently the “D”-term contributions, are insignificant. Finally, the strongly 2PA-allowed ($\epsilon$) states of cyanine-like dyes are well separated in energy from $S_1$ ($E_{ge} \gg E_{ee}$); resulting in “T”-terms that are small relative to the “N”-term.\textsuperscript{6}

Moreover, besides large $|\text{Re}(\gamma_0)|$, cyanines exhibit several other optical properties potentially well suited to AOS. The well-spaced excited states and the narrow absorption bands mean that one can choose a dye for which $E_{ge}$ is only a little higher than the photon energy of interest, $h\nu$. By carefully choosing the dye and photon-energy combination, one can potentially exploit near-resonance enhancement of $\text{Re}(\gamma_0)$ (which is maximised as $h\nu$ approaches $E_{ge}$) without incurring either linear loss through 1PA into $S_1$; 2PA into $S_2$ (i.e., $2h\nu < E_{ge}$), or vibronically assisted 2PA into $S_1$ ($2h\nu > E_{ee}$). For AOS at telecommunications wavelengths (1.3–1.55 $\mu$m), these criteria can be met by choosing dyes with $S_0 \rightarrow S_1$ absorptions at ca. 700–1200 nm. Chain length and/or the charge-stabilising terminal groups can be used to engineer absorptions into this range,\textsuperscript{13} although very long-chain polymethines can exhibit “symmetry-breaking” phenomena, whereby they no longer exhibit cyanine-like spectra.\textsuperscript{13–17} Chalcogenopyrylium-terminated polymethines\textsuperscript{16,18–22} exhibit some of the lowest-energy absorptions for a given chain length, and heptamethines such as 1Cl (Scheme 1) have particularly promising solution linear and nonlinear optical properties for AOS.\textsuperscript{23}

However, high-chromophore density films are required for practical applications and the aggregation that occurs under such conditions can lead to broadening of the absorption bands and to the creation of new states,\textsuperscript{24} both of which can impair the 1PA and 2PA transparency, as well as lead to light scattering. We have attempted to suppress aggregation effects in chalcogenopyrylium-terminated polymethines using Fréchet-type dendrons, but with only limited success.\textsuperscript{25} More effective is the incorporation of moderately large but out-of-plane organic substituents in “end” (R in Scheme 1), “back” (R’, and “front”, i.e., meso, substituents; some of these dyes, such as 4Clz Scheme 1), exhibited an unprecedented combination of large $|\text{Re}(\chi^{(3)})|$, large $|\text{Re}(\chi^{(3)})/\text{Im}(\chi^{(3)})|$, and small linear optical loss at 1.55 $\mu$m.\textsuperscript{26,27} The substituents and counterion used also resulted in good solubility in low-polarity high-index solvents suitable for liquid-core optical fiber applications.\textsuperscript{28}

Recently we have found that Pd[PPP$_3$]$_2$Cl groups can be rather easily introduced into the meso-positions of a variety of polymethine dyes by treatment of the corresponding Cl-substituted dyes with Pd[PPP$_3$]$_4$, and that these groups are very effective in disrupting intermolecular $\pi$-interactions, as demonstrated crystallographically, by absorption spectra of films, and for an anionic dye, by third-order NLO measurements.\textsuperscript{29} Similar reactions may be used to introduce bulky palladium-based...
substituents to perylene diimide\textsuperscript{29,30} or BODIPY\textsuperscript{31} cores, also leading to suppression of \textit{x}-stacking in the solid state.

Here we apply the same metallation reaction to \textit{meso}-chloro chalcogenopyrylium-terminated heptamethines (Scheme 1). We experimentally and theoretically compare the effects of Cl, Pd(PPh\textsubscript{3})\textsubscript{2}Cl, and Ni(PPh\textsubscript{3})\textsubscript{2}Cl substituents on molecular-level linear and nonlinear optical properties, and then examine the impact of these bulky \textit{meso}-groups on intermolecular interactions. Finally we show that one example exhibits promising optical properties for AOS in a high-chromophore density film.

Results and discussion

Synthesis

As in our previous report on other classes of heptamethines\textsuperscript{29}, Pd(PPh\textsubscript{3})\textsubscript{2}Cl-substituted dyes could be obtained from the room-temperature reaction\textsuperscript{32} of the corresponding \textit{meso}-chloro dyes with Pd(PPh\textsubscript{3})\textsubscript{4} (Scheme 1) under inert atmosphere, followed by column chromatography on silica gel. The Cl-precursor 1Cl is commercially available (as IR1061); the other chloro dyes were obtained either by counterion metathesis (1Cl\textsubscript{23}) or by condensation of the appropriate 4-methylchalcogenopyrylium salt (some of which are previously reported\textsuperscript{26,33,34} and others of which were newly synthesised) and the appropriate \textit{meso}-chloro-substituted aniline-terminated pentamethine,\textsuperscript{29} again followed by counterion metathesis (see ESI\textsuperscript{‡} for details).

One example of a Ni(PPh\textsubscript{3})\textsubscript{2}Cl derivative, 1Ni, was obtained in an analogous way using Ni(PPh\textsubscript{3})\textsubscript{4}; although less thermally stable (see ESI\textsuperscript{‡}) than 1Pd, this compound could still be obtained in good yield after purification by column chromatography. Extension of the reaction to Pd(PPh\textsubscript{3})\textsubscript{4} was more challenging: although an absorption attributable to a trace of the desired compound, due to either stronger \textit{\sigma}\textsuperscript{-}acceptor qualities. Electrochemical data (Table 1 and Fig. S8, ESI\textsuperscript{‡}) are consistent in that metallation much more significantly affects the reduction potentials than the oxidation potentials. It is worth noting also that the oxidations of 1Pd and 1Ni are electrochemically reversible, in contrast to that of 1Cl; this may be a steric effect, as in previous work on the stability of

Solution spectra

Absorption spectra for the metallated dyes and their chloro precursors were acquired in chloroform solution. All exhibit a strong and narrow cyanine-like feature, with a pronounced vibronic shoulder, in the near-IR, and only relatively weak absorption features in the visible. The variations in absorption maxima, \(\lambda_{\text{max}}\), for the 1–5Pd series follow those in the corresponding 1–5Cl species (see discussion below), but \(\lambda_{\text{max}}\) for each of the Pd(PPh\textsubscript{3})\textsubscript{2}Cl derivatives synthesised is hypsochromically shifted by ca. 600 cm\textsuperscript{-1} relative to that of its Cl precursor (see Table S1, ESI\textsuperscript{‡}). The Ni(PPh\textsubscript{3})\textsubscript{2}Cl derivative, 1Ni, exhibits an even larger hypsochromic shift of ca. 750 cm\textsuperscript{-1} relative to 1Cl. These blue shifts (Fig. 1 and Table 1) are consistent with those seen in our previous report of palladated cationic and anionic heptamethines and are qualitatively reproduced by SAC-Cl/HF/cc-pVQZ excited-state calculations (see below and ESI\textsuperscript{‡})\textsuperscript{29}. The \textit{S}_0 \rightarrow \textit{S}_1 transitions of cyanine-like polymethines, including, according to the calculations, the present metallated examples, are generally well-approximated as HOMO-to-LUMO excitations; accordingly, the effect of polymethine chain substituents on the energy of the strong \textit{S}_0 \rightarrow \textit{S}_1 absorption can be rationalised by considering the inductive and resonance effects of the substituents on the HOMO and LUMOs.\textsuperscript{37,38} Depending on the choice of the charge-stabilising end group and the number of methine units, the \textit{meso} methine unit sits on a nodal plane perpendicular to the molecular plane for either the HOMO or the LUMO. For both the present chalcogenopyrylium species and the classes of heptamethines used in our previous report on Pd(PPh\textsubscript{3})\textsubscript{2}Cl-substituted dyes,\textsuperscript{23,38–41} the \textit{meso} position lies on a nodal plane in the HOMO (i.e., it is an “unstarred” position in the terminology of the Dewar–Knott rules\textsuperscript{32,41}). Thus, the blue shift suggests that M(PPh\textsubscript{3})\textsubscript{2}Cl substituents primarily destabilise the LUMO relative to that of the corresponding Cl compound, due to either stronger \textit{\pi}\textsuperscript{-}donor properties and/or weaker \textit{\sigma}\textsuperscript{-}acceptor qualities.

Electrochemical data (Table 1 and Fig. S8, ESI\textsuperscript{‡}) are consistent in that metallation much more significantly affects the reduction potentials than the oxidation potentials. It is worth noting also that the oxidations of 1Pd and 1Ni are electrochemically reversible, in contrast to that of 1Cl; this may be a steric effect, as in previous work on the stability of

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**Scheme 2** Structures examined computationally in this work.

**Fig. 1** UV-vis-NIR absorption spectra of Cl- and M(PPh\textsubscript{3})\textsubscript{2}Cl-substituted thioipyrylium-terminated heptamethines in chloroform solution.
the radical dications formed by oxidation of cationic cyanines, where even replacing Me by Et groups can have dramatic effects.44

DFT (ωB97X-D/cc-pVDZ) calculations for model compounds (Scheme 2 and Fig. 2; Fig. S3 and S4 in the ESI) confirm the expected nodal properties of the frontier orbitals and indicate, consistent with electrochemistry, that it is indeed the LUMO energy that is more significantly affected by metallation, and that Ni(PPh3)2Cl has a slightly more destabilising effect than Pd(PPh3)2Cl (or Pt(PPh3)2Cl). Moreover, metal d-orbital contributions to the LUMO (and the HOMO−1) are also evident for the metallated species. They also indicate that the HOMO–LUMO gap for the chloro species is lower than that of the analogous species in which the Cl is replaced by H, consistent with what is seen for indole-terminated heptamethines.26 The DFT polymethine C–C bond lengths also change subtly from Cl to M(PPh3)2Cl derivatives, consistent with the M(PPh3)2Cl substituents acting as stronger π-donors than the Cl atom (the thiopyrylium−C10 and C9−C9 bonds slightly shorten and the Cα−C3 and Cβ−C7 bonds lengthen; see Table S2 in the ESI‡).

In addition to the meso-substituent, the “end” (R) substituent and the choice of chalcogen are also known to affect the spectra of dyes of this type, whereas the “back” (R′) group has little effect (as seen here comparing 2Cl to 1Cl, or 2Pd to 1Pd); within the series 1Cl−5Cl and 1Pd−5Pd (see Table 2 and Table S1, ESI‡) these effects are consistent with previous literature work. Replacement of “end” (R) phenyl groups with alkyl or out-of-plane aryl groups is known to result in a significant blue shift,21,26 whereas increasingly heavy chalcogens result in successive red shifts.14,19,23,26 These two effects more-or-less cancel when comparing 1Cl/2Cl to 1Cl or 1Pd/2Pd to 4Pd, as previously seen in the comparison of 1Cbz to 4Cbz.26 The additional red shift seen on replacing Se with Te, largely offsets the blue shift engendered by the Pd(PPh3)2Cl meso-substituent (relative to Cl or 3,6-di-tert-butylcarbazol-9-yl groups, the latter exhibiting slightly red-shifted spectra vs. chloro, presumably as a result of limited π-donation from the out-of-plane group and/or weaker inductive electron-withdrawal abilities26), results in 5Pd exhibiting an absorption maximum (1069 nm) close to that of dyes of this type, whereas the “back” (R′) group has little effect (as seen here comparing 2Cl to 1Cl, or 2Pd to 1Pd); within the series 1Cl−5Cl and 1Pd−5Pd (see Table 2 and Table S1, ESI‡) these effects are consistent with previous literature work. Replacement of “end” (R) phenyl groups with alkyl or out-of-plane aryl groups is known to result in a significant blue shift,21,26 whereas increasingly heavy chalcogens result in successive red shifts.14,19,23,26 These two effects more-or-less cancel when comparing 1Cl/2Cl to 1Cl or 1Pd/2Pd to 4Pd, as previously seen in the comparison of 1Cbz to 4Cbz.26 The additional red shift seen on replacing Se with Te, largely offsets the blue shift engendered by the Pd(PPh3)2Cl meso-substituent (relative to Cl or 3,6-di-tert-butylcarbazol-9-yl groups, the latter exhibiting slightly red-shifted spectra vs. chloro, presumably as a result of limited π-donation from the out-of-plane group and/or weaker inductive electron-withdrawal abilities26), results in 5Pd exhibiting an absorption maximum (1069 nm) close to that of dyes of this type, whereas the “back” (R′) group has little effect (as seen here comparing 2Cl to 1Cl, or 2Pd to 1Pd); within the series 1Cl−5Cl and 1Pd−5Pd (see Table 2 and Table S1, ESI‡) these effects are consistent with previous literature work. Replacement of “end” (R) phenyl groups with alkyl or out-of-plane aryl groups is known to result in a significant blue shift,21,26 whereas increasingly heavy chalcogens result in successive red shifts.14,19,23,26 These two effects more-or-less cancel when comparing 1Cl/2Cl to 1Cl or 1Pd/2Pd to 4Pd, as previously seen in the comparison of 1Cbz to 4Cbz.26 The additional red shift seen on replacing Se with Te, largely offsets the blue shift engendered by the Pd(PPh3)2Cl meso-substituent (relative to Cl or 3,6-di-tert-butylcarbazol-9-yl groups, the latter exhibiting slightly red-shifted spectra vs. chloro, presumably as a result of limited π-donation from the out-of-plane group and/or weaker inductive electron-withdrawal abilities26), results in 5Pd exhibiting an absorption maximum (1069 nm) close to that of dyes of this type, whereas the “back” (R′) group has little effect (as seen here comparing 2Cl to 1Cl, or 2Pd to 1Pd); within the series 1Cl−5Cl and 1Pd−5Pd (see Table 2 and Table S1, ESI‡) these effects are consistent with previous literature work. Replacement of “end” (R) phenyl groups with alkyl or out-of-plane aryl groups is known to result in a significant blue shift,21,26 whereas increasingly heavy chalcogens result in successive red shifts.14,19,23,26 These two effects more-or-less cancel when comparing 1Cl/2Cl to 1Cl or 1Pd/2Pd to 4Pd, as previously seen in the comparison of 1Cbz to 4Cbz.26 The additional red shift seen on replacing Se with Te, largely offsets the blue shift engendered by the Pd(PPh3)2Cl meso-substituent (relative to Cl or 3,6-di-tert-butylcarbazol-9-yl groups, the latter exhibiting slightly red-shifted spectra vs. chloro, presumably as a result of limited π-donation from the out-of-plane group and/or weaker inductive electron-withdrawal abilities26), results in 5Pd exhibiting an absorption maximum (1069 nm) close to that...
previously reported for 4Cbz (1055 nm). The similarity of absorption maxima for 3Cl (1054 nm) and 3Pd (995 nm) to those of 1Cl/2Cl (1063 nm) and 1Pd/2Pd (999 nm), respectively, suggests that the ortho-alkynyl substituent of the "end" aryl groups does not result in as effective an out-of-plane twist as the use of 2,6-Me₂C₆H₃ "end" groups.²¹

Solution nonlinear optical properties

The real and imaginary parts of the molecular-level third-order polarisabilities, Re(γ) and Im(γ), were measured at a wavelength of 1.35 μm using the Z-scan technique for 1Pd and 1Ni and compared to previously reported data for 1Cl. Trends in the Re(γ) for polymethines can often be rationalised using only the N-term of eqn (1). Indeed, the differences in Re(γ) between 1Cl and 1Pd can largely be accounted for by the higher energy, but slightly weaker, S₀ → S₁ absorption of the latter, along with reduced near-resonance enhancement in the latter case. The reduced value of |Re(γ)/Im(γ)| seen for the 1Pd species is due to both the reduced magnitude of Re(γ) and to a larger value of Im(γ), arising from a larger 2PA cross-section. The latter effect can also be attributed to the blue shift of the absorption maximum; cyanine-like dyes typically exhibit vibronically assisted S₀ → S₁ 2PA with peak transition energies ca. 0.2 eV greater than the S₀ → S₁ 1PA peak transition energy and so will more closely approach resonance with 1.55 μm photons as the 1PA is blue-shifted. Indeed, the differences in molecular NLO properties between 1Cl and 1Pd are similar to those between 1Cl and an analogue in which replacement of the phenyl substituents on the thiopyrylium moieties with tert-butyl groups is responsible for a blue shift.²⁶

The magnitude of Re(γ) for 1Ni, on the other hand, is much smaller than that for either 1Cl or 1Pd and cannot be rationalised solely by consideration of the S₀ → S₁ excitation. To investigate the origin of this effect in more detail we turned to SAC-CI/HF/cc-pVDZ excited-state calculations, from the results of which we evaluated Re(γ₀) using the sum-over-states procedure. The excited-state calculations overestimate the difference in S₀ → S₁ energies between Cl- and Pd(PPh₃)₂Cl-substituted examples and, therefore, overestimate the difference in Re(γ) (Fig. 3; Tables S3 and S4, ESI†). Nevertheless, for 1Cl and M1Pd (and M1Pt), the N-term associated with S₀ → S₁ dominates the sum-over-states value of Re(γ₀) (Table S4, ESI†). The T-terms are comparatively small since the lowest energy e′ states are 1.7–2.0 times higher in energy than S₁. On the other hand, calculations for M1Ni reveal not only a significant T-term contribution from S₁ at an energy 1.7 times that of S₀, but also from S₂ at only 1.4 times the energy of S₁; together these outweigh the N-term to afford a small positive value of Re(γ₀) (experiment affords a small negative value of Re(γ) at 1.55 μm; this discrepancy can easily arise if the calculations do not afford precisely correct relative state energies or transition dipoles). The origin of this effect is not particularly straightforward: both S₂ and S₃ of M1Ni arise primarily from linear combinations of (HOMO) → (LUMO+1), (HOMO−1) → (LUMO), and double (HOMO → LUMO) electronic excitations, as do the S₂ states of M1Cl, M1Pd, and M1Pt, and these orbitals are all typical polymethine π-orbitals to which the meso substituents make only relatively minor contributions (as shown in Fig. S3, ESI† it is the HOMO−2 and LUMO+2 in which large differences in the orbital distributions become evident between the different substituents). However, regardless of the detailed reasons for the differences between Ni(PPh₃)₂Cl- and Pd(PPh₃)₂Cl-species, the small magnitudes of Re(γ) found and calculated for the former emphasise the importance of taking into account the properties of higher lying excited states besides S₁ when identifying cyanine-like dyes for third-order NLO applications. In particular, it is important to realise that a cyanine-like molecular structure and a cyanine-like absorption spectrum do not necessarily guarantee typical cyanine-like NLO behaviour (i.e., large negative Re(γ) and, therefore, nonlinear refractive index, n₂).

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**Fig. 3** Partial state-energy diagram for Cl- and M(PPh₃)₂Cl-substituted thiopyrylium-terminated heptamethines from SAC-CI/HF/cc-pVDZ excited-state calculations. Transition moments are shown (in Debye) for the g → e (S₀ → S₁) 1PA transitions (solid arrows) and e → e′ transitions (where g → e′ are 2PA-allowed transitions).

**Fig. 4** Aggregate geometries probability distribution for M1H with BF₄⁻ (top left) and BAr⁺ (top right) counterions and for M1Pd (Cl counterion, bottom) using the same methods as our previous work.²⁶,47,48 The color scale on the lower right corresponds to the probability of finding aggre-gates, with the probability of 1 corresponding to the average bulk density of thiopyrylium pairs.
Modeling of effects on M(PPh₃)₂Cl groups on aggregation

To gain insight into the possible impact of bulky M(PPh₃)₂Cl groups on aggregation in amorphous neat films of chalcogenopyrylium-terminated dyes, we performed atomistic molecular dynamics simulations as previously described for other polymethine systems. Fig. 4 shows the probabilities of obtaining different dye–dye aggregates, defined as pairs of chromophores separated by a radial distance of 6 Å or less, for the M1H cation with BF₄⁻ and BAR₄⁻ anions and for M1Pd with Cl anions. For M1H-BAR₄⁻ the preferred aggregate geometries consist of parallel molecules with little or no lateral offset, thus approaching the ideal “H-aggregate” geometry. On the other hand, M1H-BF₄⁻ forms a much wider range of aggregate geometries. These findings are broadly consistent with absorption spectra for 1Cl and 1Cl', which are respectively blue-shifted (H-aggregate-like) and red-shifted (yet much broader than expected for simple J-type aggregation). Even with the small chloride counterion, the bulky meso-substituent of M1Pd is predicted to preclude many of the aggregate geometries adopted by M1H-BF₄⁻, including both H-aggregates and, to a large extent, J-aggregates, although the plot shows a significant probability of zero-offset aggregates clustered around a twist angle of ca. 45°, as well as the possibility of aggregates with large offsets and a variety of torsion angles.

Solid-state optical properties

Solid-state UV-vis-NIR absorption spectra were acquired for the M(PPh₃)₂Cl-functionalised dyes as both neat films and as 50 wt% blends with amorphous polycarbonate (APC). In all cases, the maxima are bathochromically shifted relative to those seen in solution, the absorption feature is considerably broader, and the vibronic shoulder is increased in relative absorbance. Nonetheless, to a first approximation, the spectra of all the M(PPh₃)₂Cl-functionalised dyes are reasonably solution-like and do not show marked H- or J-aggregate-like features. In contrast, as noted above, 1Cl (Fig. 5) and 1Cl' exhibit spectra that strongly deviate from those found in solution. The Pd(PPh₃)₂Cl group in 1Pd is also more effective in narrowing the absorption band in the solid than the bulky and rigidly out-of-plane 3,6-di-tert-butylcarbazol-9-yl meso-substituent in the previously reported 1Cbz, which exhibits a significant J-aggregate-like low-energy shoulder in solid films (Fig. 5). In our previous work, the 3,6-di-tert-butylcarbazol-9-yl group was more efficient at affording solution-like spectra in films when combined with a bulky “back” (R' in Scheme 1) substituent, such as the tert-butyl group used in 4Cbz and, more importantly, in combination with out of plane tertiary alkyl “end”-substituents (R in Scheme 1). Moreover, in contrast to 4Cbz and related compounds, 1Pd is accessible through two simple steps (counterion metathesis and reaction with Pd(PPh₃)₄) from a commercially available material (1Cl, IR1061). Even 1Pd (only a single step from 1Cl) exhibits a solution-like spectrum, although the use of the smaller BF₄⁻ counterion results in a broader overall absorption than that of 1Pd (Table 2). The tert-butyl substituent of 2Pd has little impact on the solid-state spectra. The out-of-plane “end” groups of 3Pd-5Pd result in absorption bands in neat films (Table 2) that are slightly narrower than those of the compounds with Ph “end” groups (R) or than that of 4Cbz (for which FWHM = 2880 cm⁻¹).

Linear optical losses were also measured for selected films of 1:1 blends with APC at 1550 nm using a prism coupler (Table 2). Of the blends examined, the loss for 1Pd (which also exhibits the broadest absorption band) is the highest. The values for the other blends fall in a similar range to those for some previous examples of chalcogenopyrylium-terminated polymethines with bulky meso-substituents (e.g., 8.5 and 4.4 dB cm⁻¹ for 1Cbz and 4Cbz, respectively, as 1:1 blends with APC), although they are all somewhat higher than the best previously reported values (3.3–3.5 dB cm⁻¹ for thiopyrylium examples with tertiary alkyl “end” groups, a tert-butyl “back” group, and a 3,6-di-tert-butylcarbazol-9-yl meso-substituent). Finally, the real part of the third-order susceptibility, Re(χ(3)), for a 1:1 5Pd:APC blend was measured using the Z-scan method to be -3 × 10⁻¹¹ esu, a value which is close to that of -3.3 × 10⁻¹₁ esu previously found for a 1:1 blend of 4Cbz (which, as noted above, exhibits similar linear spectra to 5Pd) and APC. The 2PA figure-of-merit, |Re(χ(3))/Im(χ(3))|, was estimated to be greater than 10 (cf. a value of 12 for 4Cbz). These values, combined with the optical loss values of 6.3 dB cm⁻¹, suggest that, with further optimisation of processing and film
High-chromophore-density films. A Pd example with telluropyrylium termini exhibits solid-state NLO properties and linear loss values that are promising for use. However, dye–dye interactions in the solid state, as previously demonstrated for other classes of dyes. Metal substitution does not affect the cyanine-like character of the absorption spectra. For a Pd example, the third-order NLO properties are typically cyanine-like, but for a Ni example, the magnitude of the nonlinearity is considerably reduced owing to the contributions of a low-lying 2PA state, illustrating that chromophores with cyanine-like absorption spectra do not necessarily also exhibit cyanine-like NLO properties. A Pd example with telluropyrylium termini exhibits solid-state NLO properties and linear loss values that are promising for use in near-IR all-optical switching applications.

Conclusions
M(PPh$_3$)$_2$Cl-functionalisation of chalcogenopyrylium-terminated polymethines is an effective means of reducing dye–dye interactions in the solid state, as previously demonstrated for other classes of dyes. Metal substitution does not affect the cyanine-like character of the absorption spectra. For a Pd example, the third-order NLO properties are typically cyanine-like, but for a Ni example, the magnitude of the nonlinearity is considerably reduced owing to the contributions of a low-lying 2PA state, illustrating that chromophores with cyanine-like absorption spectra do not necessarily also exhibit cyanine-like NLO properties. A Pd example with telluropyrylium termini exhibits solid-state NLO properties and linear loss values that are promising for use in near-IR all-optical switching applications.

Conflicts of interest
There are no conflicts of interest to declare.

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References


32 We have also found that the same reagent, Pd(PPh$_3$)$_4$, can also catalyse the Stille reaction of meso-Cl dyes, including 4Cl, with 9-tributylstannyl]anthracene derivative in the presence of CuI at elevated temperatures (ref. 27). Presumably species such as 4Pd are intermediates in the catalytic cycle.


35 The $^{31}$P spectrum of 5Pd in CHCl$_3$ consists of only a singlet, presumably due to a coincidence in the chemical shifts of the two resonances. However, two doublets are seen in other solvents (e.g., in CD$_2$Cl$_2$: $\delta$ 16.4 (d, $J_{pp} = 305$ Hz), 15.1 (d, $J_{pp} = 304$ Hz)).


41 Ref. 23 and 39 show frontier molecular orbitals for chalcogenopyrylium-terminated heptamethines, which are similar to those obtained here for M1Cl, M1Ni, M1Pd, and M1Pt. Ref. 39 and 40 show MOs previously calculated for indoline, benzothiazole, and dicyanomethylene-terminated polymethines, which serve as models for the benzoindoline, naphthothiazole, and “TCF”-terminated species studied in ref. 29, with the understanding that the HOMOs of mono-, penta-, nona-, and tridecamethines will have the same nodal properties as one another and as the LUMOs of tri-, hepta-, and undecamethines, the LUMOs of the former class will resemble the HOMOs of the latter, and that TCF-terminated heptamethines are effectively C(CN)$_2$-terminated tridecamethines.


