Little is known about the molecular pathway to monomers of semiconductor nanocrystals. Here we report a general reaction pathway, which is based on hydrogen-mediated ligand loss for the precursor conversion to 'monomers' at low temperature before nucleation. We apply $^{31}$P nuclear magnetic resonance spectroscopy to monitor the key phosphorous-containing products that evolve from $MX_n + E = \text{PPh}_2H + \text{HY}$ mixtures, where $MX_n$, $E = \text{PPh}_2H$, and HY are metal precursors, chalcogenide precursors, and additives, respectively. Surprisingly, the phosphorous-containing products detected can be categorized into two groups, $\text{Ph}_2\text{P}-\text{Y}$ and $\text{Ph}_3\text{P}(\text{E})-\text{Y}$. On the basis of our experimental and theoretical results, we propose two competing pathways to the formation of $M_2E_n$ monomers, each of which is accompanied by one of the two products. Our study unravels the pathway of precursor evolution into $M_2E_n$ monomers, the stoichiometry of which directly correlates with the atomic composition of the final compound nanocrystals.
Colloidal semiconductor nanocrystal (NC) quantum dots (QDs) with distinct properties and well-acknowledged potential in many applications such as light-emitting diodes\(^{12,13}\), lasing\(^{14}\), photovoltaics\(^{15,16}\) and bio-labelling/imaging\(^{17–19}\) have been the focus of intense research ranging from fundamental science to applied technologies. For the past two decades, there have been significant efforts made to advance NC synthesizes\(^{20–38}\). Mainly, the wet-chemical synthesis of colloidal metal chalcogenide NCs depends on the use of metal salts such as cadmium oleate (Cd(OA)\(_2\) or Cd(OOC\(_{17}H_{33}\))\(_2\)) and tri-n-octylphosphine chalcogenides (E=PC(CH\(_3\))\(_3\)) or ETOP, E=S, Se, and Te), together with beneficial additives in 1-octadecene (ODE) including diphenylphosphine (HP(C\(_6\)H\(_5\))\(_2\) or HPPh\(_2\), a secondary phosphine) ref. 33). During the induction period, the consumption of the resulting NCs\(^{17–19,21,22,36–38}\). For example, the number of recipes developed, recent studies have demonstrated that the use of commercial diphenylphosphine (HP(C\(_6\)H\(_5\))\(_2\) or HPPh\(_2\), a secondary phosphine) resulted in an equilibrium of SeTOP \(+\) HPPh\(_2\) \(\Rightarrow\) TOP + Se \(-\) PPh\(_2\)H. Meanwhile, high metal-to-se and low Se-top feed ratios were found to shift the equilibrium to the right\(^{23}\), which remarkably improved the NC synthesis with high particle yield and synthetic reproducibility at low reaction temperatures\(^{17–19,21,22,36–38}\). E \(=\) PPh\(_2\)H is much more reactive than ETOP\(^{15,23}\). The use of ETOP \(+\) HPPh\(_2\) leading to the E precursor of E \(=\) PPh\(_2\)H instead of ETOP has been shown to benefit the synthesis of NCs such as PbSe (refs 17,18) and CdSeS (ref. 38), while the direct use of Cd(OA)\(_2\) \(+\) HPPh\(_2\) \(\Rightarrow\) TOP + Se \(-\) PPh\(_2\)H. Meanwhile, high metal-to-se and low Se-top feed ratios were found to shift the equilibrium to the right\(^{23}\), which remarkably improved the NC synthesis with high particle yield and synthetic reproducibility at low reaction temperatures\(^{17–19,21,22,36–38}\). E \(=\) PPh\(_2\)H is much more reactive than ETOP\(^{15,23}\). The use of ETOP \(+\) HPPh\(_2\) leading to the E precursor of E \(=\) PPh\(_2\)H instead of ETOP has been shown to benefit the synthesis of NCs such as PbSe (refs 17,18) and CdSeS (ref. 38), while the direct use of E= PPh\(_2\)H (made from E= HPPh\(_2\)) is preferable to the synthesis of NCs such as ZnSe (ref. 19), ZnSeS (ref. 21) and CuInS\(_2\) (ref. 22). With the number of recipes developed, recent studies have demonstrated clearly that the control of precursor reactivity has a strong impact on the reproducibility, particle yield, and size and size distribution of the resulting NCs\(^{17–19,21,22,36–38}\). For example, the reactivity of thiourea precursors was shown to control the size, yield and batch-to-batch consistency of PbS NCs\(^{37}\).

Generally, the current state-of-the-art in NC synthesis is principally empirical, with little insight into the stepwise pathway by which monomers are generated. There exists ‘an induction period’ before nucleation occurs, which was briefly addressed for CdS\(_2\) \(\Rightarrow\) TOP + Se \(-\) PPh\(_2\)H. Meanwhile, high metal-to-se and low Se-top feed ratios were found to shift the equilibrium to the right\(^{23}\), which remarkably improved the NC synthesis with high particle yield and synthetic reproducibility at low reaction temperatures\(^{17–19,21,22,36–38}\). E \(=\) PPh\(_2\)H is much more reactive than ETOP\(^{15,23}\). The use of ETOP \(+\) HPPh\(_2\) leading to the E precursor of E \(=\) PPh\(_2\)H instead of ETOP has been shown to benefit the synthesis of NCs such as PbSe (refs 17,18) and CdSeS (ref. 38), while the direct use of E= PPh\(_2\)H (made from E= HPPh\(_2\)) is preferable to the synthesis of NCs such as ZnSe (ref. 19), ZnSeS (ref. 21) and CuInS\(_2\) (ref. 22). With the number of recipes developed, recent studies have demonstrated clearly that the control of precursor reactivity has a strong impact on the reproducibility, particle yield, and size and size distribution of the resulting NCs\(^{17–19,21,22,36–38}\). For example, the reactivity of thiourea precursors was shown to control the size, yield and batch-to-batch consistency of PbS NCs\(^{37}\).

### Results

NMR study of various reaction systems. The reactions studied are presented in Fig. 1 for CdSe and Supplementary Figs 1–9 for M (II) \(\text{Se}\), Fig. 2 for CdS and Supplementary Figs 10–13 for CdS and ZnS, and Fig. 3 for CdTe and Supplementary Figs 14–21 for GeTe. Figure 4 is for Cu-Se, In-Se, and CuInSe, and Supplementary Figs 22–23 are for Cu-Se, In-Se, and CuInSe. Figure 5 deals with [Cd(Se_2PPh_2)]_2 (3) + Cd(OA)_2 + HY for the demonstration of equation 2, which leads to CdSe_2 + as shown by Supplementary Fig. 25 and which is supported by Supplementary Fig. 24 with the reaction of [Cd(Se_2PPh_2)]_2 (3) + Cd(OA)_2 + HY + HPPh_2. On the basis of our in situ \(^{31}\)P NMR monitoring of a large number of reactions dealing with six metal cations (M) and three chalcogenes (E) in the presence of the five types of HY additives, we propose a conceptual pathway...
(Fig. 6) that demonstrates the probable reactions from precursors to monomers. This distinct pathway starts with the coordination of n E=PPh2H molecules per MXn, followed by the H-mediated ligand loss of n HX molecules to result in one M(EPPh3)n (A). Afterwards, A undergoes dimerization to D that reacts with HY to E and/or F, or reacts with HY leading to B and/or C that undergoes dimerization to E and/or F, respectively. M2En and 1 are then produced from E (equation 1), while M2En and 2 from F (equation 2). Metathesis equilibria are involved, in which there are reversible exchanges of small ligand molecules, HPPh2, E=HPPh2 and HY (around metal chalcogenide centres, such as D + HY=⇌ E=E=PPh2H and D + HY=⇌ F+HPPh2), and chalcogenide exchange reactions such as 1+Se=PPh2H⇌2+HPPh2, which affect the detection of 1, 2 and HPPh2. The chalcogenide exchange equilibria were examined by density functional theory (DFT) shown in Supplementary Table 2 and Supplementary Note 2. Furthermore, we performed extensive DFT calculations for the probable isomers of the intermediates A–F shown in Fig. 6; therefore, we are able to elucidate further the pathway we proposed in Fig. 7, in which the probable isomers with detailed bonding skeletons of each intermediate A–F are illustrated, providing a much deeper understanding.

Figure 1 presents our 31P NMR spectra collected from four representative mixtures of Cd(OA)2 + SeTOP + HPPh2 (a) and with the additional additives of oleylamine (C18H35NH2, b), dodecylthiol (C12H25SH, c) and dodecylalcohol (C12H25OH, d). It is Se=PPh2H rather than SeTOP that reacts with Cd(OA)2 because of SeTOP + HPPh2⇌Se=PPh2H+TOP (refs 15,23). The products 1a (PbP–OC17H33) and 1b (PbP–PPh2) equilibrate via PbP–COOR (1a) + HPPh2⇌RCOOH + PbP–PPh2 (1b), which is weighted to the right at room temperature (RT)21,24. The additional products of 2a (PbP(Se)–OC17H33) and 2b (PbP(Se)–PPh2) from the mixtures of Cd(OA)2, Zn(OA)2 or Ge(OA)2 + Se=PPh2H are shown in Supplementary Figs 3–5. The addition of a primary amine C18H35NH2 to the mixture of Fig. 1a, as shown in Fig. 1b, resulted in additional 1c (PbP–NH2C18H33) and 2c (PbP(Se)–NH2C18H33). The use of the thiol C12H25SH generated 1d (PbP–SC12H25) without the detection of 1a and 1b (Fig. 1c). Similarly, the use of the alcohol C12H25OH produced 1e (PbP–OC12H25) and 2e (PbP(Se)–OC12H25; Fig. 1d). The same P-containing compounds were observed from the mixtures with Pb(OA)2 replacing Cd(OA)2 (Supplementary Fig. 5), which strongly suggests that Compounds 1a–e (PbP–Y) have their own similar pathways (for different Y), and Compounds 2a–e (PbP(Se)–Y) have their own similar pathways (for different Y). Thus, we propose that Compounds 1 and 2 follow two different paths for their formation from their own immediate precursors (Figs 1 and 2).

The temporal evolution of the absorption of growing CdSe NCs (shown in Supplementary Figs 6–7) suggests that the amount of additives, thiol C12H25SH or alcohol C12H25OH affects nucleation/growth, in addition to other experimental parameters such as the temperature and amount of HPPh2 used. Focusing on the identification of the reaction pathway before nucleation, the present study does not address the control of the size and size distribution, which could be affected by various experimental parameters including cation-to-anion feed molar ratios and the nature of Se=PR2H as shown by Supplementary Figs 8 and 9. In addition, the size and size distribution of the CdSe NCs synthesized with SeTOP + HPR2 (dicyclohexylphosphine (or HPCy2) and HPPh2) are different from those with Se=PPh2H and Se=PPh2H. Previously, the reaction of Cd(OA)2 + Se=PPh2H was reported to lead to Compound Cy2P–OC17H33 (1a analogue) and Cy3P(Se)–OC17H33 (2a analogue)24. Therefore, the present study on the general reaction pathway
from precursors to $M_{2}E_{2}$ monomers before nucleation at low reaction temperatures should benefit the field by leading to a better understanding of the 'induction periods' to tailor, optimize and manipulate nucleation/growth, which offers finer control of the size and size distribution of NCS produced.

Figure 2 shows our $^{31}$P NMR spectra collected from four representative mixtures of Cd(OA)$_2$ + S = PPh$_2$H (a) and with the additional additives of oleylamine (C$_{18}$H$_{35}$NH$_2$, b), dodecylthiol (C$_{12}$H$_{25}$SH, c) and dodecylalcohol (C$_{12}$H$_{25}$OH, d). The chalcogenide S is generally less reactive than Se and Te under QD formation conditions$^{10–12}$. Rather than employing an in situ generation of Se = PPh$_2$H (Fig. 1 and Supplementary Figs 1–9) or Te = PPh$_2$H (Fig. 3 and Supplementary Figs 14–21), the analogue S = PPh$_2$H is sufficiently stable to be used directly (Supplementary Figs 10–13$^{21,22}$). The P-containing products detected from the S = PPh$_2$H-related reactions with Cd(OA)$_2$ (without additional HPPH$_2$ but with free HPPH$_2$ present) are similar to other chalcogenide-related reactions (Figs 1 and 3). Again, the products from the four reactions (Fig. 2) are grouped into Compounds 1 and 2. For example, the products formed are elucidated as follows: 1a without an additive (Fig. 2a), 1a and 1c with an amine additive (Fig. 2b), 1d with a thiol additive (Fig. 2c) and 1e and 1a with an alcohol additive (Fig. 2d). The major difference between the Cd + S reactions (Fig. 2) and the Cd + Se reactions (Fig. 1) is the formation of 2b (P$_2$H$_2$(P–S)–PPh$_2$) under all conditions. Compound 2b was also detected from a mixture of Zn(OA)$_2$ + S = PPh$_2$H shown in Supplementary Figs 10–12.

TeTOP is much more reactive than SeTOP and HPPH$_2$ as the Se and S precursors are shown in Fig. 4, and the other divalent metal salts of Zn, Ge and Pb studied, the same trends were discovered (Supplementary Figs 14–21). For $E$ = Se (Supplementary Figs 1–2) in the absence of additional additives, 1a and 1b were predominantly found. With amine addition, 1c and 2c are also formed. With thiol addition, 1d is formed as a main product, and with alcohol addition, both 1e and 2e are formed. For $E$ = S, 1a–e were detected along with 2b (Supplementary Figs 10–13). For $E$ = Te, none of Ph$_2$P(Se–Y) but 1a–e were observed (Supplementary Figs 14–21). Thus, for all the combinations investigated, the reaction of $M_{2}X_{2} + E = PPh_{2}H + HY$ appeared to follow equation 1 to produce 1 and/or equation 2 to produce 2 along with the formation of $M_{2}E_{2}$ monomers.

More interestingly, the detection of P-containing compounds for Cu (I) and In (III) is similar to that for $M_{2}E_{2}$ (II). C$_{12}$H$_{25}$SH has been used as a solvent and a ligand to improve the synthesis of CuInSe$_2$ and CuInS$_2$ QDs$^{22,29–31}$. Representative $^{31}$P NMR data for the synthesis of Cu$_2$Se, In$_2$Se$_3$ and CuInSe$_2$ using Se = PPh$_2$H and S = PPh$_2$H as the Se and S precursors are shown in Fig. 4, and for the synthesis of CuS, In$_2$S$_3$ and CuInS$_2$ in Supplementary...
The asterisk (*) is complexed to Cd (ref. 23).

Experiments were performed at RT for 15 (1), 30 (2), 45 (3) and 60 min (4) for 2c (Fig. 4b) leads to the product HPPh₂ being weighted towards the right (Supplementary Fig. 2, Supplementary Note 2), similar to TOP weighted towards the right (Supplementary Table 2 and Supplementary Note 2). As mentioned before, the equilibrium of PH₂P–SC₁₂H₂₅ is formed (refs 21, 23–25), except for 2e (with the amine, thiol and alcohol, but not with the acid). According to the previous study on 3 + Cd(OA)₂ (ref. 24), it is reasonable that the presence of HPPh₂ could speed up equation 2. As shown by Supplementary Fig. 24, the catalytic amount of HPPh₂ (0.05 eq. based on 3) accelerated significantly each of the three reactions, with 2 still being the main product. With more HPPh₂ (1.00 eq. based on 3), additional 1c (with 1b), 1d (with 1a and 2a) and 1e were detected, respectively. Thus, HPPh₂ could also initiate another equation 1 to 1 + Cd₂Se₂ (via A (Cd₂Se₂P₂H₂) as shown in Supplementary Fig. 25). The results shown by Fig. 5 and Supplementary Fig. 24 clearly support that the equilibrium of 1e + Se = PPh₂H ⇄ 2e + HPPh₂ is weighted towards the right, which is in agreement with our DFT examination shown in Supplementary Table 2 and Supplementary Note 2.

Figure 6 presents a schematic interpretation of our experimental results (shown in Figs 1–5 and Supplementary Figs 1–9). When a mixture of metal carboxylate and chalcogenide TOP compound (ETOP) was mixed with dialkylphosphine such as HPPh₂ with or without the presence of additives such as amines, thiols and/or alcohols, the formation of NCs begins with chalcogenide exchange, namely ETOP + HPPh₂ ⇄ TOP + E = PPh₂H (refs 15, 23–25), the exchange of which activates the chalcogenide. Subsequently, the activated E = PPh₂H reacts by...
coordinating the chalcogenide atom to the metal centre (equation 3). In the absence of HPPH$_2$, the diocytphosphine impurity in TOP could play the same chemical function, which was only realized recently.$^{15,17-23}$

$$MX_n + nE = \text{PPh}_2H' \rightarrow X_n M (E = \text{PPh}_2H')_n$$

$$X_n M (E = \text{PPh}_2H')_n \rightarrow M - (\text{EPPh}_2H)_n (A) + nH' - X$$

Following the coordination (equation 3), as experimentally demonstrated by Fig. 4e, intermediate A ($M - (\text{EPPh}_2H)_n$) is formed, accompanied by H−X (equation 4). It seems reasonable that the H−P bond of $E = \text{PPh}_2H$ is strong enough to sustain the coordination to the metal, but weak enough for H to leave and to form HX. The chalcogen coordination to the metal not only increases the acidity of the P-bound H but also makes H accessible to the adjacent X group. Thus, in the forward reaction direction, the P-bound H leads to the elimination of the ligand X resulting in A and HX (equation 4). In the next step, we propose A reacts with HY first to give B and/or C, which then dimerize towards E and/or F, respectively. At the same time, A could first dimerize towards D, [$M - (\text{EPPh}_2H)_n$], and then reacts with HY to give E and/or F. For example, dimer D reacts with HY to produce $E = \text{PPh}_2H + M_2E_n + \text{Ph}_2P - Y$ (1; equation 5) or HPPH$_2 + M_2E_n + \text{Ph}_3P(E) - Y$ (2; equation 6). Our proposed pathway leading to the observation of 1 and 2 significantly differs from the pathway proposed in 2010 (ref. 15), as detailed in Supplementary Fig. 26 and Supplementary Note 3. One major difference is intermediate A and its formation and subsequent evolution (equations 3–6), which were not

![Figure 4](image-url)
the use of amine, the trend of which is in agreement with that shown in Fig. 1. The relevant pathway to the formation of monomers and 2 is shown in Supplementary Fig. 25.

Figure 5 | 31P NMR spectra of reaction mixtures of 3 + 6Cd(OA)2 + HY. (a) 16RNH2, (b) 4RSH, (c) 16ROH. The slowest disappearance of 3 occurs with the use of amine, the trend of which is in agreement with that shown in Fig. 1. The relevant pathway to the formation of monomers and 2 is shown in Supplementary Fig. 25.

Figure 6 | Schematic of the general pathway for formation of M2Emerson monomers. For simplicity, this figure is drawn for M (II) only at low temperature from metal carboxylic acid (MX2) and dialkylphosphine chalcogenide (E=PPh2H) with the use of additive HY. Specific schemes for the other metal valences can be constructed accordingly. E = S, Se or Te. When HY = COOH (a), HPPH2 (b), RNH2 (c), RSH (d) and ROH (e), Compounds 1 and 2 are labelled as 1a–e and 2a–e, respectively. The equilibrium of 1 + E=PPh2H ⇌ 2 + HPPH2 is worthy of notice (Supplementary Table 2 and Supplementary Note 2). Note that another secondary phosphine, dicyclohexylphosphine (HPCy2), was also tested (as shown in Supplementary Figs 1 and 3); precursor E=PCy2H instead of E=PPh2H also leads to Compound Cy2P–Y (I) and Cy2P(E)–Y (2). The correlation between the reactivity of E=PR2H (with R = Ph or Cy) and the size of resulting NCs is the subject of another study. The dotted box is for a system to start from single-source precursors (such as 3 shown in Supplementary Fig. 25 with E = Se and M = Cd (II)). See Supplementary Fig. 26 and Supplementary Note 3 for the difference of the putative mechanisms proposed by ref. 15 and by the present study. With Y = PPh2, intermediate D in nature is F. Here two competing pathways are proposed for the formation of M2Em Emerson monomer: one is A-(B or D)-E-1 + M2Em, the other is A-(C or D)-F-2 + M2Em.

addressed in the work of 2010 but are clearly elucidated in the present study. Note that the pathway proposed in 2010 does not address at all the detection of 1b (PPh2–PPh2, 14 p.p.m.) from the reactions of Pb(OA)2 + Se=PPh2H and Cd(OA)2 + Se=PPh2H at RT.

Figure 6 is formulated for the case of M (II), but also applies to M (I) and M (III) where their monomers are accordingly proposed to be M2E and M2Em, respectively. Obviously, A and B are connected by equilibrium A + HY ⇌ B + E=PPh2H, while A and C by A + HY ⇌ C + HPPH2. Consequently, B and C are correlated by B + E=PPh2H ⇌ C + HPPH2, similarly to Compounds 1 and 2 by 1 + E=PPh2H ⇌ 2 + HPPH2.

These equilibria are clearly affected by the relative amount of HPPH2, E=PPh2H and HY. The formation of the monomer M2E occurs via the ligand loss of I from intermediate E (equation 1) and/or 2 from intermediate F (equation 2). With Y = PPh2, intermediate D in nature is F; thus, D can result in 2b + M2Em (equation 2).

DFT study. To further understand the fundamental chemistry involved in the putative pathway proposed in Fig. 6, let us turn our attention to the possible isomers with their bonding skeletons of each of the intermediate species A to F proposed in Fig. 6. In addition to metal ions (M), chalcogenides (E) and diphenylphosphinio species (Ph2P), intermediates B to F contain the various Y groups. Consequently, each intermediate has multiple possible constitutional isomers, while most possible combinations of bonds, such as P–E, E–E, P–P, P–Y and E–Y bonds, exist in well-known compounds, and all such bonds can in principle coordinate to metal ions leading to multiple possibilities. For example, for Y = NHR in Fig. 6, the N could bond to Cd, P or Se; if N is bound to P, two bonding arrangements (M–P–N and M–N–P) could in principle be expected. These uncertainties are amenable to DFT calculations, which provide useful information to minimize positional isomers, with the cancellation of errors in the DFT approximation. In this way, the calculated bonding trends should be reliable. The possibilities in Fig. 7 are distinguished by DFT calculations at the M06//B3LYP/6-31++G (d,p) Stuttgart/Dresden (SDD) level in ODE media. Our DFT-calculated structures and energies of many more possible isomers are shown in Supplementary Tables 3–25 including structural, geometric and rotational isomers. An additional description and discussion of the isomers of each intermediate A to F can be found immediately before Supplementary Tables 3–17.
The most stable A is with the P–Se–Cd–Se–P skeleton among the seven isomers computed (Supplementary Table 3). For the two predominant species B1 and B2 found, they have the Se–Cd–P–Y and P–Se–Cd–Y skeletons, respectively. B1 versus B2 includes P–Y versus M–Y bonds, without E–Y bonds. With \( Y = \text{NHR} \) for CdSe (Supplementary Table 4), the B1 isomer was calculated to be 10.1 kJ mol\(^{-1}\) (free energy \( \Delta G \)) more stable than B2. This energy trend of B1 < B2 was not found for the other Y. For \( Y = \text{SR} \) (Supplementary Table 4), the distinction is quite clear that the direct metal-bound B2 isomer P–Se–Cd–SR was calculated to be 82.5 kJ mol\(^{-1}\) more stable than the B1 isomer with Se–Cd–P–SR. For \( Y = \text{OR} \) (Supplementary Table 5), the B2 isomer with the P–Se–Cd–OR skeleton was found to be at the lowest energy, but the B1 isomer with the Se–Cd–P–OR skeleton was only 6.9 kJ mol\(^{-1}\) higher—an energy difference that is close to the accuracy of the DFT method and could be affected by the exact nature of various R groups, the solvent used and the temperature employed. For \( Y = \text{OOCR} \) (Supplementary Table 6), the directly metal-bound B2 isomer is 111.3 kJ mol\(^{-1}\) more stable than the B1 isomer with Se–Cd–P–OOCR. For \( Y = \text{PPh}_2 \) (Supplementary Table 6), B2 is 58.7 kJ mol\(^{-1}\) more stable than B1.

Intermediate C with an extra chalcogen E atom compared with intermediate B evidently has more constitutional possibilities. Intriguingly, the connectivity follows similar patterns to that of intermediate B. For \( Y = \text{NHR} \) (Supplementary Table 7), C1 with the Se–Cd–Se–P–N connectivity has the lowest energy. Note that there is an extra Se inserted between the Cd and P atoms. The most stable Cd–N-bound species C2 was found to contain the four-membered N–Cd–Se–P–Se–(Cd\(^{\ast}\)) ring, which was 18.7 kJ mol\(^{-1}\) calculated. For \( Y = \text{SR} \) (Supplementary Table 8), C2 with a direct Cd–SR bond is favoured much more than the other isomers considered. Complexes with this C2-type connectivity but with \( Y = \text{SSPPh}_2 \) have been characterized experimentally\(^{35}\). For \( Y = \text{OR} \) (Supplementary Table 9), C1 and C2 differ by only 2.3 kJ mol\(^{-1}\) and can therefore be considered iso-energetic. For \( Y = \text{OOCR} \) (Supplementary Table 10), C2 with the direct Cd–OOCR bonding is much more stable, similar to the case of \( Y = \text{SR} \).

Consequently, for \( Y = \text{NHR} \), B1 and C1 are preferred. For \( Y = \text{OR} \), the selectivity is not obvious. For \( Y = \text{SR} \) and OOCR, B2 and C2 are favoured. Thus, the preference on the bonding skeleton calculated for intermediates B and C is similar. The nature of the chalcogenide also affects the relative stability of B1 versus B2 (Supplementary Table 18) as well as that of C1 versus C2 (Supplementary Table 19). For \( Y = \text{NHR} \) specifically, B2 and C2 are stabilized for \( E = \text{S} \), whereas B1 and C1 are more stable for \( E = \text{Te} \) than for \( E = \text{Se} \). For CdSe, our preliminary efforts on the kinetics associated with the putative pathway \( A + H \rightarrow B + \text{Se}=\text{PPh}_2\text{H} \) are presented in Supplementary Figs 28–31 and Supplementary Note 5 with A1b for A and B2a for B. The trend of the kinetics computed seems to be in agreement with our experimental data showing the slowest disappearance of SeTOP (Fig. 1) and of 3 (Fig. 5) is from the batch with HY = \text{RNH}_2.

Intermediates E and F are proposed as the very immediate precursors leading to monomers \( M_2E_2 \) with Compounds 1 and 2, respectively. E1 could have resulted from dimerization of B1 and E2 from B2. F1 could have resulted from dimerization of C1 and F2 from C2. Again, DFT calculations were performed to address the question of whether the various Y species are bound to Cd or to Se or to P. Clearly, E and F are computationally demanding. Generally, E isomers follow the trend of B isomers, and F follows C: low-energy B isomers lead to low-energy E, and C to F. In all cases, the four-membered ring Cd–Se–Cd–Se–(Cd\(^{\ast}\)) was found by minimization. For \( Y = \text{NHR} \) (Supplementary Table 11), E1 with the P–N bond is much more stable than E2 with the Cd–N bond by \( \sim 150 \text{ kJ mol}^{-1} \). For \( Y = \text{SR} \) (Supplementary Table 11), E2 with the Cd–S bond is more stable than E1, but the difference is smaller (32.7 kJ mol\(^{-1}\)) than that (82.5 kJ mol\(^{-1}\)) of B2 versus
B1. For $Y = $OR (Supplementary Table 12), $E_1$ is much more stable than $E_2$, whereas $B_1$ is similar to $B_2$. For $Y = $OCR (Supplementary Table 13), isomers such as $E_2$ (with the Cd–Y bond) are the most stable ones found.

Intermediate F consists of two more $E$ atoms than $E$. For $Y = $NHR (Supplementary Table 14), $F_1$, with Se inserted between the Cd and P, namely Cd–Se–P–N, is 196.6 kJ mol$^{-1}$ more stable than $F_2$ with the direct Cd–N bond. For $Y = $SR (Supplementary Table 15), $F_2$ is 78.0 kJ mol$^{-1}$ more stable than $F_1$. For $Y = $OR (Supplementary Table 15), $F_1$ is 126.1 kJ mol$^{-1}$ more stable than $F_2$. For $Y = $OCR (Supplementary Table 16), $F_2$ is 78.8 kJ mol$^{-1}$ more stable than $F_1$. For $Y = $PPh$_2$, $D_2$ (a dimer of $A$) is more stable than $D_1$ (equivalent to $F_1$) by 86.6 kJ mol$^{-1}$.

Although speculative, our current proposal is that $E$ and $F$ (or possibly higher oligomers such as from the dimerization of $E$ and $F$) facilitate the release of $I_1$ and $2$, respectively. The release of Compound $I$ is more apparent from $E_1$ (via the $M$–P bond cleavage) than from $E_2$; the Cd–P bond expected for $E_1$ to lose has a length of 2.66 Å (longer than 2.58 Å in $B_1$). In addition, the release of Compound $J_1$ (a more compound from $F_1$ (via the $M$–E bond cleavage) than from $F_2$; the Cd–Se bond expected to break for $F_1$ to lose has a length of 2.74 Å (longer than 2.69 Å in C1). For the release of $I_2$ and $E_2$, respectively, it seems reasonable that the formation of a $Y$–P bond (via the interaction of $Y$ with Ph$_2$P and with Ph$_2$P(E)) could be accompanied by the cleavage of $M$–Y and $P$–E bonds$^{44}$. It has been suggested that the oligomerization to [Cd$_x$Se$_y$]($x+y$) facilitates the release of Compound 1 ($E_1$) as a more stable than 1 more stable than (ref. 24); this thermodynamic stability of [M$_2$E$_n$]$_m$ may be the driving force of the overall reaction$^{45}$.

Discussion

The molecular pathway of precursor evolution to monomers responsible for nucleation at low reaction temperature to semiconductor NCs has been recognized as a major challenge in advancing the design and synthesis of high-quality NCs with high synthetic reproducibility and particle yield. We have successfully rationalized a general reaction pathway for precursor evolution to monomers at low reaction temperatures from the mixture of $M_{x+y}$ + ETON + HPH$_2$P + HY or $M_{x+y}$ + E = PPH$_2$H + HY. On the basis of the experimental and computational investigations, we propose the monomer of $M_2E_n$ and its formation accompanied by the loss of $Y$ atoms of monovalent, divalent or trivalent, three chalcogenides and five types of additive HY (of carboxylic acid, dialkylphosphine, amine, thiol or alcohol) results in the P-containing products of $P_{x+y}$–$Y$ (1) and $P_{x+y}$–E$–Y$ (2) via two competing pathways. Experimentally, the combination of six monovalent ions of monovalent, divalent or trivalent, three chalcogenides and five types of additive HY (of carboxylic acid, dialkylphosphine, amine, thiol or alcohol) results in the P-containing products of $P_{x+y}$–$Y$ (1) and $P_{x+y}$–E$–Y$ (2). The in-depth interpretation of the mechanism is supported by our DFT calculations. Our proposed pathway features a series of H-mediated ligand loss/exchange reactions triggered by dialkylphosphine chalcogenides (such as $E = $PPH$_2$) to form intermediate A ($M$ = (E = PPH$_2$)$_n$), which leads to intermediate E (YP$_2$–M–E = PPH$_2$Y, equation 1) and intermediate F (YP$_2$–M = PPH$_2$Y, equation 2). The formation of which consists of dimerization and reaction with HY. The dissociation of ligand 1 from E and ligand 2 from F results in $M_2E_n$ monomers. Clearly, HY participates in the formation of monomers and thus could accelerate nucleation; meanwhile, a large amount of HY plays the role of a solvent and, thus, could retard nucleation. Importantly, the general pathway applies to metal chalcogenide NCs made from both toxic metals such as Cd (II) and Pb (II) and more benign metals such as Cu (I), Zn (II) and In (III). The insights into the chemical nature of the $M_2E_n$ monomer the building block, could provide the basis for the field to enable the manipulation of the chemical processes for rational design and synthesis of a variety of NCs with complex stoichiometry. The use of secondary phosphines together with beneficial additive HY should be a general and practical avenue to engineer metal chalcogenide NCs at low reaction temperatures with high quality, enhanced synthetic reproducibility and particle yield. We anticipate that the insights gained on the molecular pathway for precursor evolution into various types of $M_2E_n$ monomers may enable the field to synthesize sophisticated NCs, including phase-change materials, with better-controlled chemical processes via cation exchange as well as doping and co-doping with monovalent and trivalent metal ions$^{46–52}$. We are actively exploring the correlation between the pathway of monomer formation with the formation of magic-size and regular QDs, aiming at the control of product properties including the size and size distribution. In addition, we believe that similar to the endevour of the development of organic syntheses, the basic chemistry reported embraces the advance of the NC synthesis from an empirical art to science with pathway-enabled design leading towards the full realization of the NC potential$^{53–55}$.

Methods

$^{31}$P NMR measurements. $^{31}$P NMR was performed on a Bruker AV III 300 spectrometer operating at 161.98 MHz, referenced with an external standard, 85% H$_3$PO$_4$. Usually, we used $D_1 = 2$ s (64 scans total taking ~3 min; unless mentioned otherwise). NMR samples were usually prepared and loaded in NMR tubes in a glovebox and properly sealed. All chemicals used are commercially available from Sigma-Aldrich and were used as received (or otherwise specified). The used ligands and additives are oleic acid (OA, tech. 90%), dialkylphosphine (HPPH$_2$, 99%), 1,2-dodecanethiol (C$_{12}$H$_{25}$SH, 98%), and lauryl alcohol (C$_{12}$H$_{25}$OH, 98%). The elemental chalcogens used are sulfur (S, precipitated, Anachemia), selenium (Se, 200 mesh, 99.9999%, Alfa Aesar) and tellurium (Te, 200 mesh, 99.9%). For the assignment of Compounds 1 and 2, sodium hydride (NaH, 98%, dry), chlorodiphenylphosphine (Ph$_2$P–Cl, 97%, Alfa Aesar) were used. Compounds 1 (Ph$_2$P–Y) and 2 (Ph$_2$P(E)–Y) detected with NMR are related to the formation of monomers/solutes/NCs, and have been used to explore the formation of monomers since 2006 (refs 13,15,23–25). The P-containing products detected with $^{31}$P NMR are listed as follows: 1a (Ph$_2$P–OOC–C$_{12}$H$_{25}$), 1b (Ph$_2$P–PPh$_2$), 1c (Ph$_2$P–NHC$_{12}$H$_{25}$), 1d (Ph$_2$P–SC$_{12}$H$_{25}$), 1e (Ph$_2$P–OC$_{12}$H$_{25}$), 2a (Ph$_2$P–E)–OOC–C$_{12}$H$_{25}$, 2b (Ph$_2$P(E)–PPh$_2$), 2c (Ph$_2$P(E)–NHC$_{12}$H$_{25}$), 2d (Ph$_2$P(E)–SC$_{12}$H$_{25}$) and 2e (Ph$_2$P(E)–OOC–C$_{12}$H$_{25}$).

Computational. Our DFT calculations were performed using Gaussian 09, with ethyl groups (–C$_2$H$_5$) applied to represent the alkyl group of C$_{12}$H$_{25}$COO$^-$, C$_{12}$H$_{25}$NH$^-$, C$_{12}$H$_{25}$S$^-$ and C$_{12}$H$_{25}$O$^-$; no simplicity was applied for the phenyl group of –PPh$_2$. Full geometry optimizations were carried out to locate all of the stationary points via a hybrid B3LYP functional method with the SDD basis set and the corresponding effective core potential for the Cd, Se and Te atoms, and the all-electron 6–31++G(d, p) basis set for the other atoms of C, H, O, N and S, namely B3LYP/6–31++G(d, p), SDD. The use of effective core potential and all-electron basis was the same as before$^{15}$. Systematic harmonic frequency calculations were performed to ensure that all the structures obtained are true minima on the potential energy surfaces. A polarized continuum model (PCM-SMD) with dielectric constant $\varepsilon = 2.0$ was utilized to simulate the solvent effect of ODE via a hybrid MN06 functional method with the same basis sets as mentioned above by performing single-point calculation on the optimized structures at the B3LYP/6–31++G(d, p), SDD level. namely MN06//B3LYP/6–31++G(d, p), SDD. The charges and dominant occupancies of natural bond orbitals have been analysed with the help of the natural bond orbital analysis.

Data availability. The authors declare that all relevant data supporting the findings of this study are available from the authors on request.

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Competing financial interests: The authors declare no competing financial interests.

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How to cite this article: Yu, K. et al. General low-temperature reaction pathway from precursors to monomers before nucleation of compound semiconductor nanocrystals. Nat. Commun. 7:12223 doi: 10.1038/ncomms12223 (2016).

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