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A thirty-fold photoluminescence enhancement induced by secondary ligands in monolayer protected silver clusters†

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In this paper, we demonstrate that systematic replacement of the secondary ligand PPh₃ leads to an enhancement in the near-infrared (NIR) photoluminescence (PL) of [Ag₂₉(BDT)₁₂(PPh₃)₄]^{3−}. While the replacement of PPh₃ with other monophosphines enhances luminescence slightly, the replacement with diphosphines of increasing chain length leads to a drastic PL enhancement, as high as 30 times compared to the parent cluster, [Ag₂₉(BDT)₁₂(PPh₃)₄]^{3−}. Computational modeling suggests that the emission is a ligand to metal charge transfer (LMCT) which is affected by the nature of the secondary ligand. Control experiments with systematic replacement of the secondary ligand confirm its influence on the emission. The excited state dynamics shows this emission to be phosphorescent in nature which arises from the triplet excited state. This enhanced luminescence has been used to develop a prototypical O₂ sensor. Moreover, a similar enhancement was also found for [Ag₅₁(BDT)₁₉(PPh₃)₃]^{3−}. The work presents an easy approach to the PL enhancement of Ag clusters for various applications.

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Introduction

Monolayer protected atomically precise clusters of noble metals with systematic variation in properties belong to a new category of precision materials.^{1–3} Their distinct luminescence and characteristic electronic absorption have fascinated the scientific community for the past few years.^{4–6} The ability to crystallize them has led to a detailed understanding of their structures and this has promoted in-depth studies of their properties by computational methods.^{7–9} Among the properties of such systems, observable luminescence, especially in the near-infrared (NIR) window, has been fascinating due to its chemical and biological applications.^{10,11} Depending on the structure, composition and core size of the clusters, luminescence can be observed in different spectral regions (visible, NIR and infrared).^{12–14} The electronic structure of the metal–ligand interface is known to be a crucial factor in determining the emission properties.^{15,16} Consequently, ligand modification has been shown to result in an enhancement in luminescence.

^{17,18} The PL enhancement of Au₂₅(PET)₁₈ (PET: 2-phenylethanethiol) is a good example where ligand modification was done using 4-*tert*-butylbenzyl mercaptan (SBB).¹⁹ Also, Au₂₂(SG)₁₈ (SG: glutathione) displayed high luminescence after surface reconstruction.^{20,21} Surface modification can be made *via* the formation of ion pairing which helps in improving the PL intensity as in the case of [Ag₂₉(BDT)₁₂(PPh₃)₄]^{3−} (BDT: 1,3-benzenedithiol) which showed more than ten-fold PL increment in the presence of bulky counter ions.²² The composition of the core also influences the luminescence intensity significantly. The most dramatic aspect of this effect was the observation of a 200-fold enhancement in PL after the addition of 13 Ag atoms in the Au₂₅ cluster.²³ Also, a huge emission enhancement was observed in [Ag₂₉(BDT)₁₂(PPh₃)₄]^{3−} and [Ag₂₅(2,4-DMBT)₁₈][−] (DMBT: 2,4-dimethyl benzenethiol) clusters upon doping of Pt and Au atoms.^{24–26} [AuAg₂₄(DMBT)₁₈][−] and [Au_xAg_{29−x}(BDT)₁₂(PPh₃)₄]^{3−} exhibited ~25 and ~26 fold higher PL, respectively, compared to that of the corresponding undoped clusters. Doping of the Pt atom in [Ag₂₉(BDT)₁₂(PPh₃)₄]^{3−} resulted in a 2.3 fold PL enhancement. The nature of solvent also plays an important role in PL enhancement.²⁷ An example of this is [PtAg₂₄(DMBT)₁₈]^{2−}, which showed a 100 fold greater QY in acetonitrile compared to that in dichloromethane.²⁸

Aggregation-induced luminescence enhancement (AIE) has been proposed to be the driving force for the enhanced luminescence in biological structures, organic luminogens

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and metal nanoclusters.^{21,29–32} In such cases, non-covalent interactions between the molecules restrict the intermolecular motion which affects the luminescence (enhancement or quenching). The AIE is observed in $\text{Au}_2\text{Cu}_6(\text{S-Adm})_6(\text{PPh}_2\text{Py})_2$ (S-Adm: adamantane thiol), $\text{Au}_4\text{Ag}_{13}(\text{DPPE})_4(\text{DMBT})_9$ (DPPE: 1,2-bis(diphenylphosphino)ethane), $\text{Au}_4\text{Ag}_5(\text{DPPM})_2(\text{SR})_6(\text{BPh}_4)$ (DPPM: 1,1-bis(diphenylphosphino)methane), *etc.*^{33–35} A recent report by Zhu *et al.* suggested that the addition of excess PPh_3 in $[\text{Ag}_{29}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$ can induce aggregation, which resulted in a 13-fold PL improvement (from 0.9% QY to 11.7% QY).³⁶ The PL intensity can also be tuned by changing the temperature. The lower the temperature, the lower is the molecular motion and hence the higher is the PL intensity. $[\text{Ag}_{29}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$ displayed an ~ 25 fold greater QY at a lower temperature.³⁶

Besides the silver clusters protected with one type of ligand exclusively, such as $[\text{Ag}_{25}(\text{2,4-DMBT})_{18}]^-$,³⁷ $[\text{Ag}_{44}(\text{4-FTP})_{30}]^{4-}$ (FTP: 4-fluoro thiophenol),³⁸ $[\text{Ag}_{59}(\text{2,5-DCBT})_{32}]^{3-}$ (2,5-DCBT: 2,5-dichloro benzenethiol),³⁹ $\text{Ag}_{32}(\text{SG})_{19}$,⁴⁰ *etc.*, clusters are also known to exist with different types of ligands. Among them, one ligand provides stability to the cluster, called the primary ligand, while the other one enhances the stability and ease of crystallization of the cluster, called the secondary ligand. Such a category of clusters include $[\text{Ag}_{29}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$,⁴¹ $[\text{Ag}_{51}(\text{BDT})_{19}(\text{PPh}_3)_3]^{3-}$,⁴² $[\text{Ag}_{16}(\text{DFBT})_{14}(\text{DPPE})_4]$ (DFBT: difluoro benzenethiol),⁴³ $[\text{PtAg}_{28}(\text{S-Adm})_{18}(\text{PPh}_3)_4]^{2+}$,⁴⁴ $[\text{Ag}_{67}(\text{2,4-DMBT})_{32}(\text{PPh}_3)_8]^{3+}$,⁴⁵ $\text{Ag}_{374}(\text{SR})_{113}\text{Br}_2\text{Cl}_2$,⁴⁶ $\text{Ag}_{50}(\text{DPPM})_6(\text{TBBT})_{30}$ (TBBT: *t*-butyl benzenethiol),⁴⁷ *etc.* In the experiment here, we have demonstrated that a systematic change in the secondary ligand can lead to an unprecedented PL enhancement, creating a new handle for property modification in this class of materials. $[\text{Ag}_{29}(\text{BDT})_{12}(\text{PPh}_3)_4]^{3-}$ and $[\text{Ag}_{51}(\text{BDT})_{19}(\text{PPh}_3)_3]^{3-}$ clusters have been used to demonstrate this effect. PPh_3 ligands are replaced by *para*-substituted PPh_3 ligands such as tri(*p*-tolyl)phosphine (TTP), tris(4-fluorophenyl)phosphine (TFPP) and tris(4-chlorophenyl)phosphine (TCPP) as well as diphosphines such as DPPM, DPPE and DPPP (1,3-bis(diphenylphosphino)propane) to prepare the above-mentioned clusters.

In the discussion below, the clusters have been given short labels to simplify the text. The structure, stability, electronic and optical properties of diphosphine-protected Ag_{29} have been studied by DFT and time-dependent DFT (TDDFT) calculations. The Kohn–Sham (K–S) molecular orbitals (MOs) have also been calculated to study the contributions of atomic orbitals. A ~ 30 fold enhancement in quantum yield (QY) was observed upon replacement of PPh_3 by DPPP which makes it possible to develop useful devices. The PL enhancement of the Ag_{29} cluster by this method is much higher than that in previous reports.^{22,24,25,36} We have also shown the use of enhanced luminescence for the sensing of O_2 in the solution and solid states. This sensitivity, in turn, is shown to be due to the fact that the luminescence observed is phosphorescent in nature. Though phosphorescence emission has been observed for several gold clusters, it has not been reported for silver clusters to date.^{48,49}

Experimental

Chemicals and materials

1,3-Benzenedithiol (BDT, $\geq 99\%$), sodium borohydride (NaBH_4 , 95%) and 1,1-bis(diphenylphosphino)methane (DPPM, 97%) were purchased from Sigma-Aldrich. Silver nitrate (AgNO_3), 1,2-bis(diphenylphosphino)ethane (DPPE), 1,3-bis(diphenylphosphino)propane (DPPP), tri(*p*-tolyl)phosphine (TTP), tris(4-fluorophenyl)phosphine (TFPP) and tris(4-chlorophenyl)phosphine (TCPP) were purchased from Rankem Chemicals. Triphenylphosphine (PPh_3 , 98%) was purchased from Spectrochem. Dichloromethane (DCM), dimethylformamide (DMF) and methanol (MeOH) were purchased from Rankem and were of HPLC grade. Deuterated solvents, dimethyl sulfoxide- d_6 (DMSO-d_6) and CDCl_3 were purchased from Sigma-Aldrich. All solvents and chemicals were used without further purification.

Synthesis of $[\text{Ag}_{29}(\text{BDT})_{12}]^{3-}$ (Ia**) and $[\text{Ag}_{29}(\text{BDT})_{12}(\text{X})_4]^{3-}$, where X is PPh_3 , DPPM, DPPE, DPPP, TTP, TFPP and TCPP, labelled as **Ib**, **II**, **III**, **IV**, **V**, **VI** and **VII**, respectively**

The clusters **Ia** and **Ib** were synthesized by a reported method.⁴¹ A similar synthetic methodology was used to synthesize **II**, **III** and **IV** with some modifications, as explained in the ESI.† The addition of DPPM, DPPE and DPPP to **Ia/Ib** also resulted in the formation of these clusters. For the synthesis of **V**, **VI** and **VII**, the ligand exchange (LE) method was followed starting from **Ib**. Details are discussed in the ESI.†

Synthesis of $[\text{Ag}_{51}(\text{BDT})_{19}(\text{X})_3]^{3-}$, where X is PPh_3 , DPPM, DPPE, DPPP, labeled as **VIII, **IX**, **X** and **XI**, respectively**

The cluster **VIII** was synthesized by adopting an already reported method which has been discussed thoroughly in the ESI.†⁴² The **IX**, **X** and **XI** clusters were synthesized by the LE method starting from **VIII** using DPPM, DPPE and DPPP. Detailed procedures are given in the ESI.†

Characterization

UV–vis spectra were obtained using a PerkinElmer Lambda 25 spectrometer in the range of 200–1100 nm. Mass spectrometric measurements were done using a Waters Synapt G2-Si high-resolution mass spectrometer. Samples were measured using electrospray ionization (ESI) in the negative mode. PL measurements were performed using a HORIBA JOBIN YVON Nano Log instrument. The bandpass for excitation and emission was set at 3 nm. Dynamic light scattering (DLS) data were measured using the Malvern Zetasizer Nano ZSP instrument using a DMF solution of the clusters. X-ray photoelectron spectroscopic (XPS) measurements were carried out with an Omicron ESCA Probe spectrometer with polychromatic Al K α X-rays ($h\nu = 1486.7$ eV). The samples (DCM/DMF solution) were drop-casted on an XPS sample stub and dried under ambient conditions. During the measurement, the pass energy for survey scans was kept at 50 eV and changed to 20 eV for specific regions. Binding energies (BE) of the core levels were calibrated with C 1s BE set at 285 eV. NMR spectra were obtained using a Bruker 500 MHz NMR spectrometer (using

DMSO- d_6 and $CDCl_3$ solvents). Time-resolved spectroscopic data were collected by time-correlated single photon counting (TCSPC) with an excitation source of a LifeSpec-ps picosecond diode-laser-pumped fluorescence spectrophotometer from Edinburgh Instruments (Livingston, UK). Picosecond excitation pulses from a picoquant diode laser were used at 409 nm with an instrument response function (IRF) of ~ 50 ps. A micro channel-plate-photomultiplier tube (MCP-PMT; Hamamatsu Photonics, Kyoto, Japan) was used to detect the photoluminescence from the sample after dispersion through a monochromator. The observed fluorescence transients were fitted by using a nonlinear least-squares fitting procedure to a function with F900 software from Edinburgh Instruments.

The quality of the curve fitting was evaluated using reduced χ^2 and residual data. This time-resolved instrument can resolve at least one-fifth of the instrument response time constants after de-convolution of the IRF. The average lifetime (amplitude-weighted) of a multi-exponential decay is expressed as:

$$\tau_{av} = \sum_{i=1}^N (c_i \tau_i)$$

The QYs were measured using dilute solutions of the clusters (0.07 absorbance at ~ 446 nm using the equation given in the ESI†). All computational details are given in the ESI†.

Results and discussion

Clusters and their characterization

The luminescence enhancement of $[Ag_{29}(BDT)_{12}(PPh_3)_4]^{3-}$ (**Ib**), co-protected with thiol (BDT) and phosphine (PPh_3), was achieved through substituting the weakly bound PPh_3 (called

the secondary ligand) by other phosphine ligands, such as TTP, TFPP, TCPP, DPPM, DPPE and DPPP (the clusters formed are labelled as **II**, **III**, **IV**, **V**, **VI** and **VII**, respectively). The detailed procedures for their syntheses are given in the ESI†. All clusters were characterized by optical absorption and ESI MS measurements. First, let us discuss the Ag_{29} clusters synthesized using homologous diphosphines, DPPM, DPPE and DPPP (**II**, **III** and **IV**). The absorption spectra of $Ag_{29}(BDT)_{12}$ (**Ia**, shown in black) and **Ib** (red) presented in Fig. 1A display a maximum at ~ 446 nm along with an absorption onset at ~ 512 nm. The as-synthesized clusters **II** (blue), **III** (pink) and **IV** (green) show very similar spectra to that of **Ia/Ib**. However, the absorption maxima of **II**, **III** and **IV** are ~ 1 , ~ 2 and ~ 6 nm blue-shifted compared to that of **Ia/Ib**, respectively, along with the broadening of the absorption bands (see Fig. 1A). The spectra suggest that **II**, **III** and **IV** possess a similar atomic structure to that of **Ib**. To confirm the atomicity of these clusters, ESI MS were obtained as shown in Fig. 1B. The number of phosphines present in the clusters is denoted by Y (Fig. 1). It is clear from Fig. 1B that all the clusters show a peak at the same position (m/z 1603) for $Y = 0$ and the maximum value of Y is 4 (except for **Ia** which does not contain any phosphine). All the cluster ions have 3^- charge state which is validated by the difference between two successive peaks present in the isotopic distributions (Fig. S1A†). The spectrum of **Ia** exhibits only one peak at $\sim m/z$ 1603 which is assigned to $[Ag_{29}(BDT)_{12}]^{3-}$, whereas the red spectrum corresponding to **Ib** consists of five peaks. The separation between two successive peaks is $\sim m/z$ 87.3 ($87.3 \times 3 = 262$), the mass of one PPh_3 ligand, in agreement with the composition of **Ib**, $[Ag_{29}(BDT)_{12}(PPh_3)_4]^{3-}$. Similarly, the difference between two successive peaks in the blue spectrum is $\sim m/z$ 128 ($128 \times 3 = 384$,

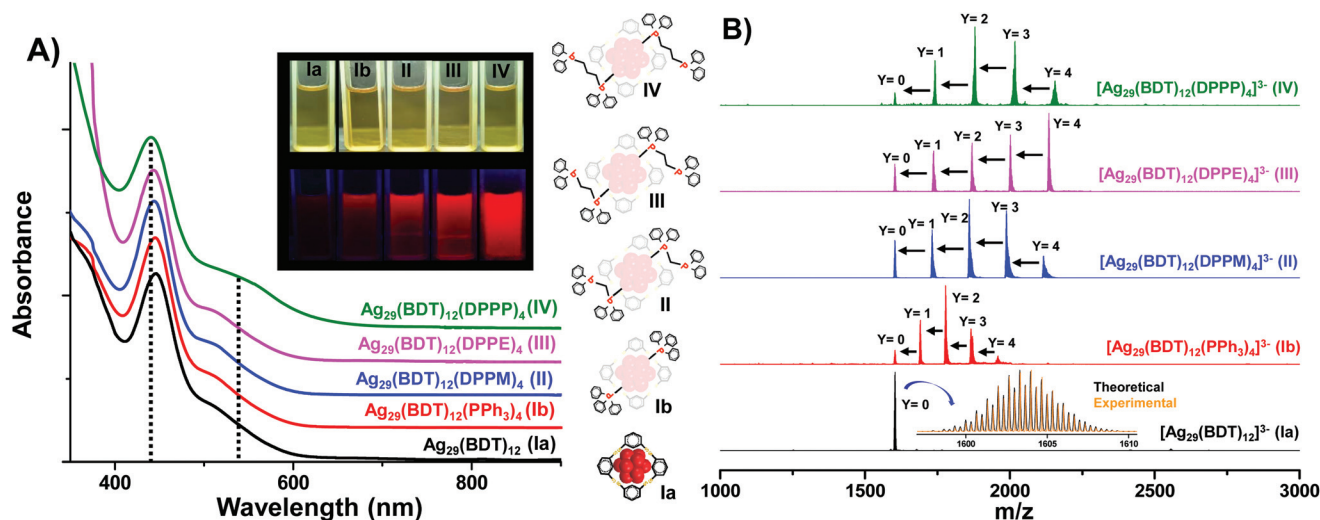


Fig. 1 UV-vis absorption spectra (A) and ESI MS (B) of **Ia** (black) and **Ib** (red), **II** (blue), **III** (pink) and **IV** (green). The absorption maximum of **IV** is ~ 6 nm blue-shifted compared to that of **Ia/Ib** and the peak at ~ 512 nm is broadened. Inset: Photographs under visible and UV light which show a gradual increase in the PL intensity. Spectra of **Ib**, **II**, **III** and **IV** are vertically shifted for clarity. On the right-hand side, schematic representations of the clusters are presented. All these clusters exhibit 3^- charge state in the ESI MS. The number of phosphines is denoted by Y . For **II**, **III** and **IV**, the maximum value of Y is 4 and all of these clusters show systematic phosphine loss. The spectral intensities of all clusters are normalized with respect to the most intense peak. An expanded view of the high-resolution spectrum of **Ia** is shown in the inset.

which matches with the mass of DPPM. For the other spectra, the peak differences are $\sim m/z$ 133 and $\sim m/z$ 137 which match with the masses of DPPE (398) and DPPP (412), respectively. Thus, from the ESI MS, it was clear that the as-synthesized clusters prepared using DPPM, DPPE and DPPP have a similar composition to that of **Ib** and were assigned as $[\text{Ag}_{29}(\text{BDT})_{12}(\text{X})_4]^{3-}$ where $\text{X} = \text{DPPM}$, DPPE and DPPP (**II**, **III** and **IV**). The molecular compositions were further proved by the high resolution spectral features which match with the theoretical spectra. The spectrum corresponding to **Ia** is shown as an inset in Fig. 1B and the spectra of other products are presented in Fig. S1B.† To prove the presence of the Ag–P bond in **Ib**, **II**, **III** and **IV** clusters, ^{31}P NMR was carried out as presented in Fig. S2.† The NMR spectra were compared with those of the corresponding phosphines. PPh_3 , DPPM, DPPE and DPPP show ^{31}P peaks at ~ -5.3 , -26.2 , -12.7 and -17.2 ppm, respectively. The corresponding clusters, **Ib**, **II**, **III** and **IV**, display peaks at ~ 1.4 , -3.3 , -0.1 , and 0.4 ppm, respectively, which affirm the formation of the Ag–P bonds. Elemental characterization of these clusters using XPS was performed (Fig. S3A†). For **Ib**, the Ag $3d_{5/2}$, S $2p_{3/2}$ and P $2p_{3/2}$ peaks appear at ~ 368.5 , ~ 162.8 and ~ 131.1 eV, respectively. For **II**, **III** and **IV**, the Ag $3d_{5/2}$ and S $2p_{3/2}$ peaks appear at the same positions as that of **Ib**. For P $2p_{3/2}$, the peak appears at a higher value of 131.5 eV. Although both Ag(0) and Ag(I) are likely to be present in the spectrum, it is hard to separate them. For diphosphine-protected Ag_{29} (**II**, **III** and **IV**), the two P atoms are different but as the energies of the Ag-bound P and the unbound P are nearly the same, it was difficult to differentiate between them. The presence of both the P atoms may be the reason for a shift of P $2p_{3/2}$ to higher BE in these samples.

Luminescence

It is well known that cluster **Ib** is extremely stable and also displays a visible luminescence. Though the cluster is weakly luminescent in the solution state, it has high luminescence in the solid state.⁴¹ However, our as-synthesized clusters (**II**, **III** and **IV**) exhibited higher PL intensity even in the solution state as shown in the inset of Fig. 1A. The luminescence profiles of these clusters are presented in Fig. 2. The black, red, blue, pink and green spectra correspond to **Ia**, **Ib**, **II**, **III** and **IV**, respectively. The clusters have almost similar concentrations as their absorbance values were the same and the absorption spectra nearly overlapped with each other. The excitation spectra (at the emission maximum of the clusters) look similar to the absorption spectra. The emission spectra are shown under ~ 446 nm excitation. The data clearly manifest the PL enhancement of **Ia** upon changing the phosphines from PPh_3 to DPPP (Fig. 2). The PL intensity of **Ib** is ~ 2 times more than that of **Ia**. Among the homologous diphosphines (DPPM, DPPE and DPPP), the long-chain ones show higher PL efficiency than that of the shorter ones and the emission maxima got shifted to a higher wavelength (bathochromic or red-shift). In the case of **Ia**, **Ib**, **II**, **III** and **IV**, emission maxima appeared at ~ 655 , ~ 655 , ~ 665 , ~ 670 and ~ 715 nm, respectively. Cluster **IV** shows the highest luminescence intensity with

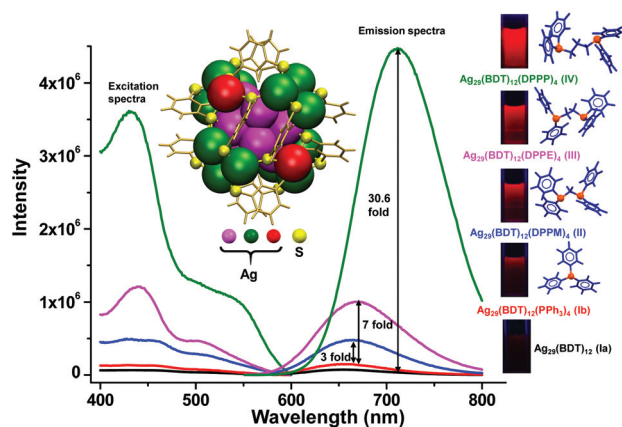


Fig. 2 Luminescence profiles of **Ia**, **Ib**, **II**, **III** and **IV** which are shown in red, blue, pink and green, respectively. Insets: The DFT calculated structure of the $\text{Ag}_{29}(\text{BDT})_{12}$ moiety (where pink, green, and red spheres denote Ag atoms; yellow sphere for S atoms; light yellow sphere for the benzene ring of thiols). The phosphine structures are presented on the right-hand side (benzene rings and P atoms are denoted by blue and orange, respectively) of the spectra along with the photographs under UV light which show a gradual increase in PL intensity. With reference to **Ib** (QY = 0.9%), QYs of **Ia**, **II**, **III** and **IV** were calculated as 0.43%, 2.9%, 6.24% and 27.5%, respectively.

the largest shift in the emission maximum. The QYs of all these clusters were calculated using the equation given in the ESI.† Considering **Ib** as a reference (QY is 0.9%),⁴¹ QYs of **II**, **III** and **IV** were 2.9%, 6.24% and 27.5%, respectively. These were enhanced ~ 3 , ~ 7 and ~ 31 fold in comparison with **Ib**. Cluster **Ia** is less luminescent than **Ib** due to the absence of any phosphine ligand (QY is 0.45%).

Computational studies

To know the reason behind the luminescence enhancement, a detailed structural investigation was needed. Although **II**, **III** and **IV** were characterized by several experimental tools, any possible changes in their structures were not clear due to the absence of crystal structures. However, theoretical calculations shed light on the structures of these clusters. The energetically most stable structure of **Ib** was derived from DFT calculations as implemented in the grid-based projector augmented wave method (GPAW) using its reported crystal structure (Fig. 3A, B, C and D).^{41,50} Then, by replacing PPh_3 ligands with different diphosphine ligands, the theoretical structures of **II**, **III** and **IV** were obtained. The geometry optimizations of all clusters were performed using the Perdew–Burke–Ernzerhof (PBE) exchange functional in real-space finite difference (FD) mode in GPAW.⁵¹ Detailed descriptions of computational methodologies are presented in the ESI.† The DFT optimized structures of **Ib**, **II**, **III** and **IV** (using the 3^- charge state) with energies of -1890.255 eV, -2263.172 eV, -2305.48 eV and -2394.88 eV are shown in Fig. 3A, B, C and D, respectively. Although the bonding distances of Ag–P (2.499–2.544 Å) for **II**, **III** and **IV** are almost very close to **Ib** (2.491 Å), the magnitude of the calculated phosphine ligand binding energies (the binding energy

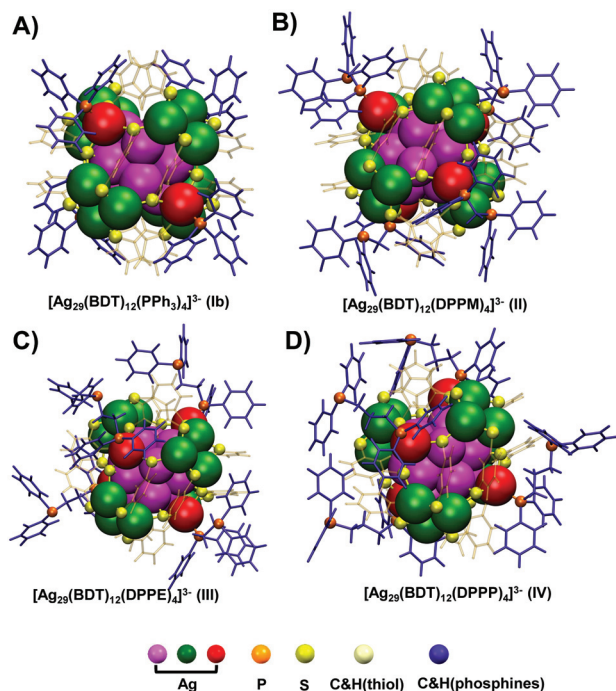


Fig. 3 The DFT calculated energetically most stable structures of **Ib** (A), **II** (B), **III** (C) and **IV** (D). The energies of **Ib**, **II**, **III** and **IV** are -1890.255 , -2263.172 , -2305.48 and -2394.88 eV, respectively. The pink, green and red denote Ag atoms; yellow denotes S atoms; orange denotes P atoms; light yellow denotes benzene rings of thiol ligands; blue denotes benzene rings and $-\text{CH}_2$ units of phosphine ligands.

is the energy difference between the total structure of the cluster and the sum of the energies of the phosphine ligands and $[\text{Ag}_{29}\text{BDT}_{12}]^{3-}$ unit of **III** (-12.25 kcal mol $^{-1}$) and **IV** (-10.21 kcal mol $^{-1}$) is higher by 3.17 kcal mol $^{-1}$ and 1.13 kcal mol $^{-1}$, respectively than **Ib** (-9.03 kcal mol $^{-1}$). Hence, clusters **III** and **IV** are theoretically more stable than **Ib**. Although the time dependent absorption spectra of **Ib** and **IV** did not show much change after 3 weeks (Fig. S3B †), the cone voltage dependent fragmentation study from ESI MS (Fig. S3C †) revealed that **IV** needed a higher voltage to detach the DPPP ligands (70 V) than those of **Ib** (40 V). This suggests the higher binding energy of DPPP than PPh $_3$ with the $[\text{Ag}_{29}(\text{BDT})_{12}]^{3-}$ unit. Also, the theoretical observation was proved by one more experiment where two bottles were taken and one of them contained **Ib** and the other one was filled with **III**. Then, small amounts of DPPE and PPh $_3$ were added to **Ib** and **III**, respectively. The absorption and emission spectra of the cluster solutions before and after phosphine addition are presented in Fig. S4. † After the addition of DPPE in **Ib**, the absorption spectrum became similar to that of **III** (Fig. S4A †). Consequently, a large enhancement in luminescence occurred (Fig. S4B †). While in the second case, where PPh $_3$ was added to **III**, the absorption and emission spectra showed hardly any change (Fig. S4C and D †). This experiment suggested that DPPE can easily substitute PPh $_3$ to form cluster **III** but PPh $_3$ was unable to replace DPPE. This is due to the

higher binding energy of **III** than that of **Ib**. The calculated binding energy of **II** (-6.89 kcal mol $^{-1}$) is lower by 2.14 kcal mol $^{-1}$ than **Ib**. However, the above-mentioned experiment was performed using DPPM which shows that the binding energy of **II** is higher than **Ib** (see Fig. S4E, F, G and H †) which resulted in the formation of **II** by addition of DPPM in **Ib**, but not the reverse.

The absorption spectra of **Ib**, **II**, **III** and **IV** were calculated using linear-response time-dependent density functional theory (LR-TDDFT) (Fig. S5 †). In this regard, the structures of these clusters were simplified by replacing each benzene ring of the phosphines by a reduced $-\text{CH}_3$ model ligand and the systems were re-optimized. 45 The solid state structures were considered during the calculation. Thus, the effect of different isomers which can coexist in the solution state was not taken into account. 52 Due to the above approximations, the theoretical spectra were slightly blue shifted as compared to the experimental ones (Fig. S5 †). The two main spectral features, the absorption maximum (peak 1) and the shoulder peak (peak 2), were identified in the theoretical spectra of **Ib**, **II**, **III** and **IV** (Fig. S5 † and Fig. 4A). In Fig. 4A, the theoretical spectra of **Ib** and **IV** were compared with the experimental spectra. For **Ib**, peak 1 at ~ 446 nm was reproduced exactly in the theoretical spectrum, but peak 2 (~ 512 nm) appeared at ~ 491 nm which is ~ 8 nm blue-shifted compared to the experimental spectrum. In the case of **II**, **III** and **IV**, peak 1 was blue-shifted by ~ 18 nm (~ 446 , 428 , 425 and 423 nm, respectively). In the lower energy range, except the two main spectral features, a few more weak peaks were observed and these were broadened as we moved from **Ib** to **IV**.

The MO transitions corresponding to peaks 1 and 2 for all clusters are given in Tables S1A and B. † In the case of **Ib**, the most intense electronic transition related to peak 1 occurred between the deeper lying occupied MO and unoccupied MO (HOMO-13 to LUMO+9). However, the most intense transition corresponding to peak 2 occurred from the frontier occupied MO to unoccupied MO (HOMO-4 to LUMO+9). For **II**, **III** and **IV**, both peak 1 and 2 arise due to the transitions from the deeper occupied MOs to unoccupied MOs (see Tables S1A and B †). The shapes of K-S MOs involved in the strongest transitions related to peak 1 and 2 of **Ib**, **II**, **III** and **IV** are shown in Fig. S6 † and Fig. 4B which confirm that the deeper occupied MOs are made up of more ligand orbitals (2s, 2p), whereas the frontier occupied MOs are having contributions from the 4d orbitals of Ag along with the ligand orbitals. On the other hand, the unoccupied orbitals are mainly composed of the 5sp orbitals of Ag. This suggests that the transitions mainly occurred *via* ligand to metal charge transfer (LMCT) and the extent of LMCT will be higher when transitions occur from the occupied MOs having a higher ligand contribution. As for **II**, **III** and **IV**, both peak 1 and 2 correspond to the transitions occurring from the deeper occupied orbitals and they display more LMCT transitions than **Ib** (here only peak 1 arises from deeper lying occupied MOs). The transitions related to the peaks arising in the lower energy (see Fig. 4A and Fig. S5 †) region also occur from the deeper occupied MOs (transitions corresponding to these peaks for **Ib** and **IV** are given in

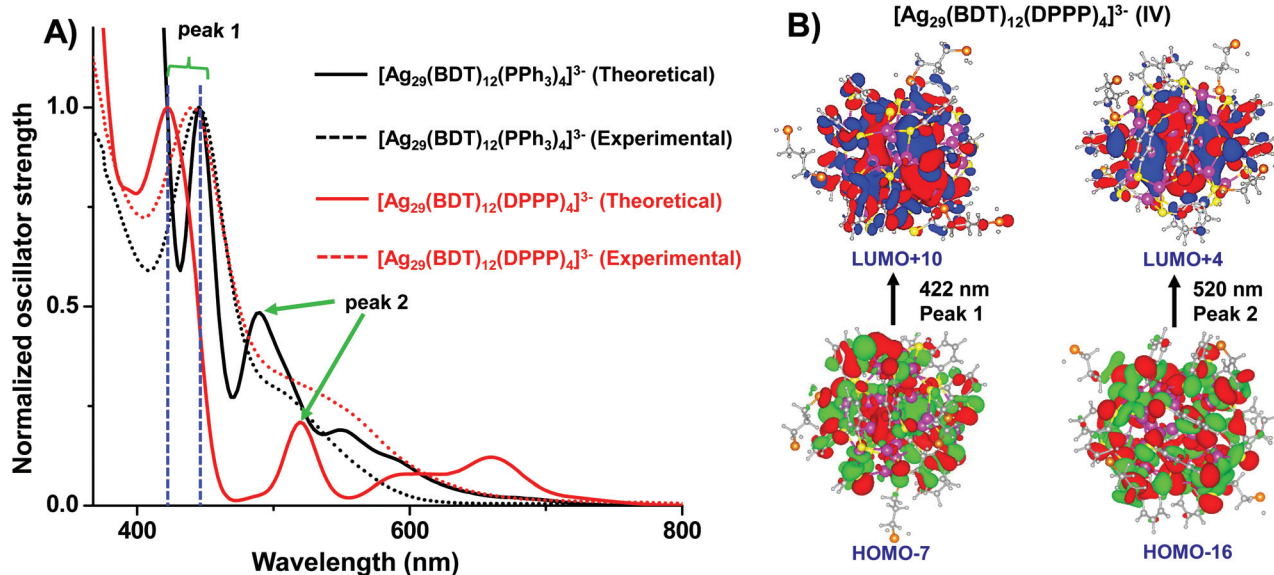


Fig. 4 (A) The theoretical absorption spectra of [Ag₂₉(BDT)₁₂(P(CH₃)₃)₄]³⁻ (black solid line) and [Ag₂₉(BDT)₁₂(P₂(CH₂)₃(CH₃)₄)₄]³⁻ (red solid line) models. The theoretical spectra are compared with the experimental spectra of **IIb** and **IV** (black and red dotted line). (B) The shape of the K-S MOs of **IV** which denotes the strongest electronic transitions related to peaks 1 and 2 (422 and 520 nm).

Table S1C†) which are more of ligand character. So, these transitions also contribute to the higher LMCT. From Fig. 4A (and Fig. S5†), we note that the lower energy peak is the most broadened for **IV**. We conclude that the highest LMCT transitions in **IV** result in a 30-fold PL enhancement.

The reason behind the luminescence enhancement

Cluster **IIb** consists of an Ag₁₃ icosahedron enclosed by four Ag₃S₆ motifs which are further capped by four Ag-PPh₃ units.^{36,41} There are six $\pi\cdots\pi$ interactions between the benzene rings of BDT ligands. There are C-H $\cdots\pi$ interactions among the benzene rings of BDT and PPh₃. The average C-H $\cdots\pi$ distance is $\sim$ 2.80 Å and $\pi\cdots\pi$ distance is 3.80 Å (see Fig. 5A). When PPh₃ ligands are substituted by DPPM ligands, the number of C-H $\cdots\pi$ interactions increase (average distance $\sim$ 3.28 Å) and also the $\pi\cdots\pi$ interactions become stronger by shortening the distance between the two benzene rings of BDT ligands ($\sim$ 3.75 Å) (see Fig. 5B). In the case of **III**, the structure becomes more asymmetric and the $\pi\cdots\pi$ interactions between the benzene rings of BDT are not the same for all the six pairs and the average distance is $\sim$ 3.79 Å. New $\pi\cdots\pi$ interactions form between the benzene rings of BDT and DPPE ligands (distance of $\sim$ 3.98 Å) and several new C-H $\cdots\pi$ interactions are observed in the structure (see Fig. 5C). The average distance of C-H $\cdots\pi$ interactions is $\sim$ 3.01 Å which is less than that of **II**. In the case of longer-chain diphosphines, the C-H $\cdots\pi$ interaction becomes feasible between sp² C-H of diphosphine and the benzene ring of BDT. Also, the distance between the two benzene rings of the neighboring BDT ligand decreases, which strengthens the $\pi\cdots\pi$ interaction in **IV** (see Fig. 5D). All these non-covalent intramolecular interactions make the diphosphine protected Ag₂₉ clusters more rigid and energetically

more stable which leads to the suppression of intramolecular vibrational and/or rotational motions (see Fig. 5). The bulkiness of the ligand is another factor which leads to a decrease in the molecular motions. This process is known as restricted intramolecular rotation or motion (RIR or RIM) of protecting ligands which help in increasing the radiative process, reducing the non-radiative processes. Generally, RIR or RIM is more feasible in the solid or crystalline state due to strong intermolecular interactions which result in stronger luminescence. Cluster **IIb** also shows high luminescence in the solid state, as mentioned earlier, but the intensity is less than that of **IV** (see photographs in the inset of Fig. S7C†). But in the diluted solution, the clusters are separated from each other by solvent molecules and the emission is weaker. The intermolecular interaction can also be expressed as aggregation which can be quantified by particle size measurement, using DLS. The sizes of **IIb** (lowest PL intensity) and **IV** (highest PL intensity) were studied and the data are presented in Fig. S7A and B.† At a higher concentration (>0.1 absorbance), aggregation occurs and thus both the clusters exhibit a larger size (Fig. S7A†). But, at a lower concentration, clusters possess a very small size ($\sim$ 2 nm) which suggests that under this condition, clusters do not show aggregation (or intermolecular interaction) (<0.1 absorbance). The PL intensities at a lower cluster concentration (shown in Fig. S7C†) reveal that even in a very dilute solution ($\sim$ 0.05 absorbance), **IV** acquires significant PL intensity while **IIb** shows hardly any emission. This suggests that the high PL intensity of **IV** in the solution state is due to the strong non-covalent intramolecular interactions and not due to aggregation or intermolecular interactions. Thus, luminescence enhancement of nanoclusters can be obtained by modifying the ligands which help in the confinement of

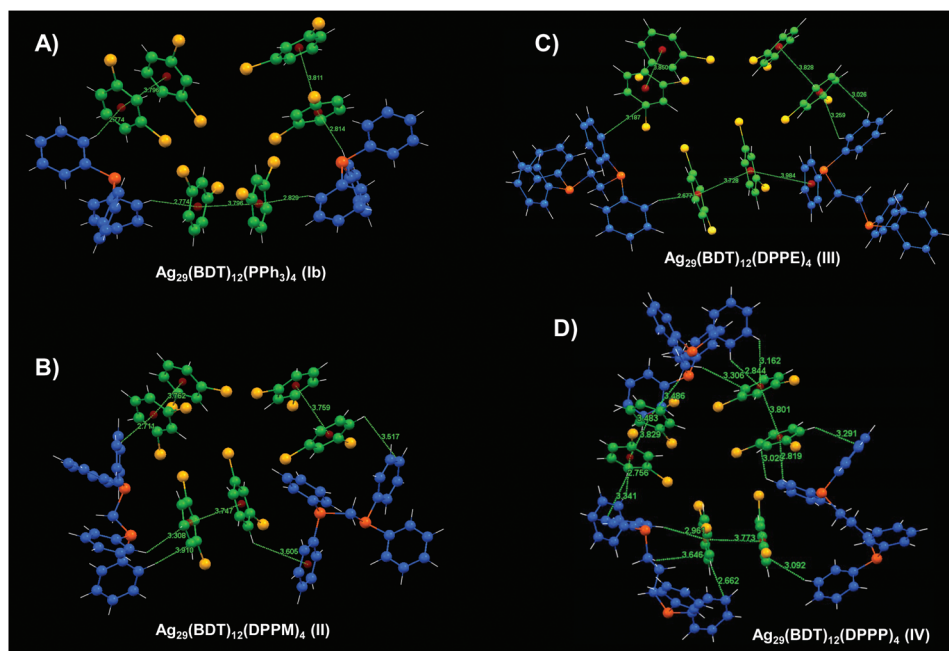


Fig. 5 Non-covalent intramolecular interactions such as the $\pi\cdots\pi$ interaction between the benzene rings of BDT ligands and the C–H $\cdots\pi$ interaction between the benzene rings of BDT and phosphine ligands of **Ib** (A), **II** (B), **III** (C) and **IV** (D). The DFT calculated structures of **Ib**, **II**, **III** and **IV** presented in Fig. 3 are considered to demonstrate the interactions. Benzene rings of BDT and phosphine ligands are shown in green and blue, respectively. Yellow and orange correspond to 'S' and 'P' atoms. All 'H' atoms are shown in white. Silver atoms are not shown.

electronic wavefunctions.¹⁵ The computational results propose that the luminescence is due to LMCT. Due to the interaction between the benzene rings of phosphine and BDT ligands, ligand to ligand charge transfer (LLCT) also takes place. As further interaction occurs between the diphosphine and BDT ligands, high charge transfer occurs for diphosphine protected clusters which helps in increasing the PL intensity. The enhanced luminescence in solution is further enhanced in the solid state due to the intercluster interaction. Along with the pronounced emission, cluster **IV** shows a ~ 60 nm red-shifted emission compared to **Ib** (Fig. 2). For **II** and **III**, emission maxima are ~ 10 and ~ 15 nm red-shifted, respectively. Also, small blue-shifts were observed in the absorption maxima of **II**, **III** and **IV** (Fig. 1A). This is mainly due to the distortion in the cluster core (Ag_{13}) arising due to the modifications of phosphine ligands (Fig. S8†). The icosahedral Ag_{13} core is highly symmetric in **Ib** (as **Ib** is having a centre of inversion, hence centrosymmetric) which is clearly manifested in Fig. S8A.† The structure looks exactly the same while viewing through the cartesian coordinates, X, Y and Z (*a*, *b* and *c*, respectively). But, the symmetry is disrupted in the case of clusters **II**, **III** and **IV** (see Fig. S8B, C and D†). Cluster **IV** exhibits a highly asymmetric core which resulted in the largest shift in the absorption and emission maxima. Due to the asymmetric metal core and ligands, the total structures of **II**, **III** and **IV** become asymmetric. In the centrosymmetric system, some of the transitions are forbidden (Laporte rule). Therefore, in the asymmetric clusters (**II**, **III** and **IV**), these forbidden transitions become allowed which result in PL enhancement.

Applications in sensing

Such luminescence has enormous utility in sensing. In the present work, this property was used for the sensing of O_2 gas which is demonstrated in Fig. 6A. Gaseous O_2 was purged through the cluster solution for a few seconds and the absorption and emission spectra were obtained which are shown in Fig. 6A (the black spectrum corresponds to **IV**). No change in the absorption spectrum was observed (blue spectrum), but the emission intensity decreased drastically. The solution was then purged with Ar which resulted in PL enhancement keeping the absorption spectrum unchanged (red spectrum in Fig. 6A). Also, N_2 and CO_2 gases were used for purging which also showed a similar kind of PL enhancement (Fig. S9A and B†). The cluster showed luminescence quenching even in the solid state upon exposure to O_2 . The inset of Fig. 6A reveals that cluster coated polystyrene shows an intense luminescence under UV light but when O_2 was exposed through a balloon, it showed luminescence quenching. With increasing O_2 concentration, the PL intensity decreased gradually (see Fig. S9C†). An investigation of the reason behind the selective sensing of O_2 by the cluster led us to the conclusion that the luminescence is actually phosphorescence in nature. Purging of N_2 , CO_2 and Ar gases helped in the removal of dissolved O_2 from the solution which resulted in PL enhancement. d^6 , d^8 and d^{10} heavy metal complexes are known to be triplet emitters (phosphorescent complexes).⁵³ These metal clusters can also be compared with their metal complexes. Due to the strong metal induced spin-orbit coupling, mixing of singlet-triplet states

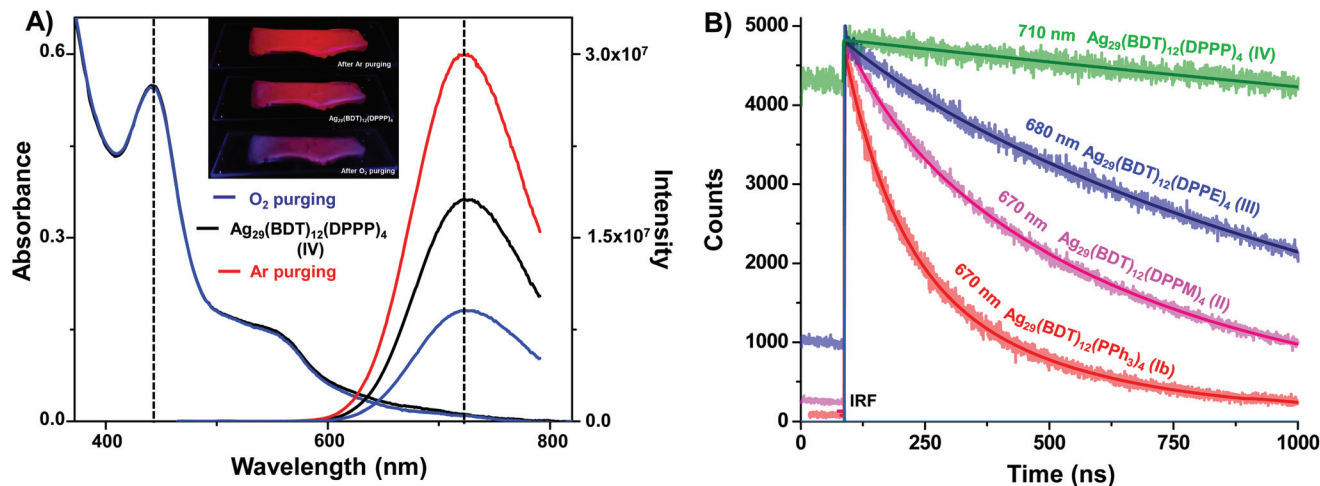


Fig. 6 (A) The optical absorption spectra and PL spectra of **IV** (black) after oxygenating and deoxygenating the cluster solution by purging O_2 (blue) and Ar (red), respectively. While the absorption spectrum does not show any change, luminescence changes drastically with and without O_2 . (B) Nanosecond resolved decay of **Ib**, **II**, **III** and **IV** at (λ_{ex} = 409 nm) for emission maxima i.e., at 670, 670, 680 and 710 nm, respectively.

increased which eliminated the spin-forbidden nature of the radiative relaxation of the triplet state, thus enhancing phosphorescence emission at room temperature. The phosphorescence wavelength, lifetime and quantum yield depend strongly on the nature of ligands. In the present work, the singlet-triplet overlap increases with an increase in carbon chain length, resulting in an enhancement of the PL intensity.

Lifetime studies

PL lifetimes of the clusters were monitored by using time resolved spectroscopy. Fig. 6B shows the PL decay transients of clusters **Ib**, **II**, **III** and **IV** at their corresponding PL maxima of ~660, ~670, ~680 and ~710 nm, respectively, using excitation at 409 nm. Cluster **Ib** shows bi-exponential fluorescence relaxation with a faster component of 99.65 ns and a slower component of 336.49 ns. The average lifetime of **Ib** is found to be 215 ns. Similarly, clusters **II** (108.44 and 589.95 ns) and **III** (120 and 1133.47 ns) exhibit two lifetime components while **IV** (6196.04 ns) displays only one lifetime component. The average lifetime for the cluster has been observed to be increased gradually from ~215 ns for **Ib** to ~6.2 μ s for **IV**. Lifetime values of all the clusters are given in Table S2 (see the ESI†). The bi-exponential decay for clusters **Ib**, **II** and **III** indicates that there is some non-radiative process along with the radiative process. As the chain length between the diphosphines increases, the contribution of the faster component decreases (51%, 17% and 4%, respectively) which corroborates that the non-radiative process is decreasing (see Table S2†). The increase in average lifetime upon ligand exchange corroborates the enhanced radiative process (phosphorescence) due to the formation of a rigid and energetically more stable cluster. In the case of phosphorescence, the radiative decay occurs from an excited triplet state back to a singlet state, where the triplet state is formed by non-radiative conversion from the excited singlet state (intersystem crossing). As spin/orbit interactions are feasible in heavy atom containing mole-

cules and thus, a change in spin is more favorable in the metal cluster. Hence, upon substituting PPh_3 by diphosphines, the rate of spin-orbit coupling increases and this leads to a reduction in the non-radiative process. So, the rate of ISC increases as phosphines are substituted by diphosphines. This finding is consistent with the results obtained by our PL and computational studies. The picosecond resolved decay of clusters was measured at their emission maxima.

PL enhancement in the monophosphine substituted clusters

To compare the PL enhancement of $[Ag_{29}(BDT)_{12}(X)_4]^{3-}$ in the presence of diphosphines and monophosphines, clusters were synthesized using *para*-substituted PPh_3 ligands such as TTP, TFPP and TCPP (**V**, **VI** and **VII**). The clusters were synthesized following the LE method explained in the ESI.† The absorption spectra of **V**, **VI** and **VII** (red, blue and pink, respectively) are shown in Fig. 7A and the data are comparable to those of **Ib** (black). The PL spectra are shown in Fig. 7B which manifest the increment of the PL intensity of the Ag_{29} cluster upon replacing PPh_3 with TTP, TFPP and TCPP. The PL enhancement of **V**, **VI** and **VII** is 3, 5 and 5 times, respectively, with respect to **Ib** (QYs are 2.7%, 4.5% and 4.5%, respectively). The ESI MS of these clusters are shown in Fig. S10,† which show the attachment of four phosphine ligands to each cluster and hence confirm their atomicity. The PL enhancement of **V** can be attributed to the increase in mass which helps in increasing the rate of intersystem crossing (ISC). Halogen atoms are known to increase the rate of the ISC process and hence PL intensities are enhanced in the case of **VI** and **VII**.

PL enhancement of $[Ag_{51}(BDT)_{19}(PPh_3)_3]^{3-}$

Similar kinds of experiments were done using another known cluster, $[Ag_{51}(BDT)_{19}(PPh_3)_3]^{3-}$ (**VIII**), having similar protecting ligands (BDT and PPh_3). We synthesized three diphosphine (DPPM, DPPE and DPPP) protected Ag_{51} clusters, **IX**, **X** and **XI** (detailed synthetic processes are given in the ESI†). The

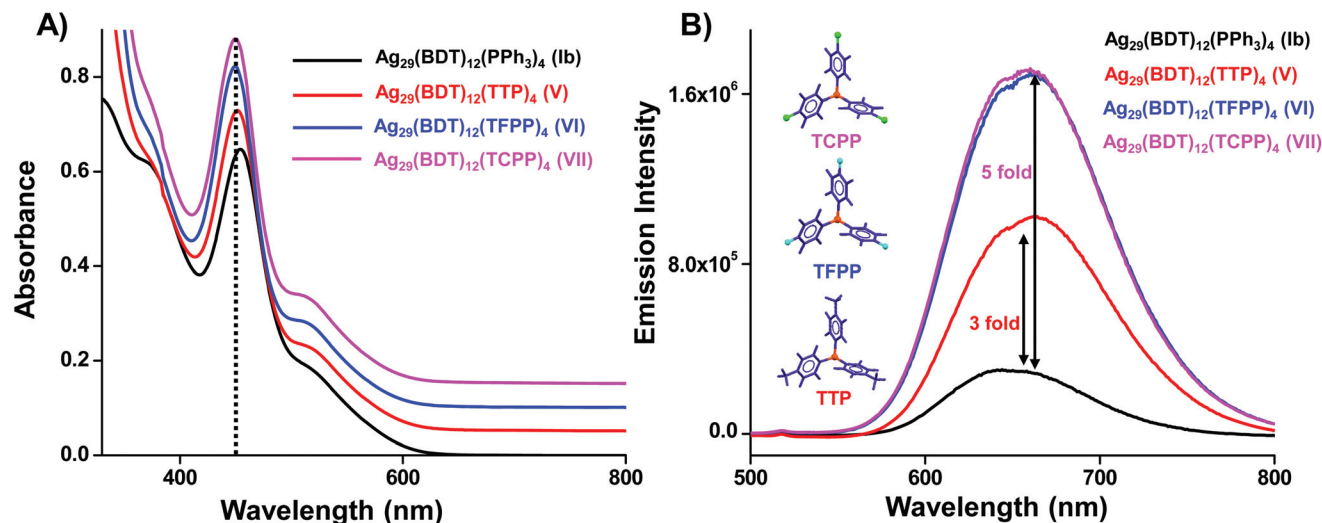


Fig. 7 (A) UV-vis absorption spectra and (B) the excitation-emission spectra (under ~ 446 nm excitation) of Ib, V, VI and VII. Cluster V shows a 3 fold PL improvement compared to that of Ib while a 5 fold enhancement was observed for VI and VII.

absorption and the emission spectra of these clusters are shown in Fig. S11,[†] which are almost similar to VIII proving that the structure and atomicity remained the same in all the clusters. The emission spectra show a 3, 7 and 17 fold PL enhancement for IX, X and XI, respectively (QYs of VIII, IX, X and XI are 0.12%, 0.35%, 0.84% and 2.04%, respectively). Cluster XI also showed PL quenching upon O_2 purging which confirms that the emission process was phosphorescence, similar to that of IV (see Fig. S12[†]).

Conclusions

In conclusion, we present the synthesis of different phosphine (DPPM, DPPE, DPPP, TTP, TFPP and TCPP) protected Ag_{29} clusters which are more luminescent than $[Ag_{29}(BDT)_{12}(PPh_3)_4]^{3-}$. The luminescence of these clusters can be perceived by the naked eye in the solution state when compared to that of $[Ag_{29}(BDT)_{12}(PPh_3)_4]^{3-}$. A detailed analysis is done for $[Ag_{29}(BDT)_{12}(DPPM)_4]^{3-}$, $[Ag_{29}(BDT)_{12}(DPPE)_4]^{3-}$ and $[Ag_{29}(BDT)_{12}(DPPP)_4]^{3-}$ using several measurements. Their structures, stability and electronic characteristics are understood from DFT and TD-DFT calculations. Absorption spectra and K-S MOs are calculated. By introducing these diphosphines, the surface rigidity of the clusters is increased via the formation of more non-covalent interactions between the ligands ($\pi \cdots \pi$ and $C-H \cdots \pi$ interactions). The rigidity of the cluster promotes the radiative transitions by increasing RIR. Hence, these clusters possess longer lifetimes (~ 215 , ~ 510 , ~ 1096 and ~ 6196 ns for PPh_3 , DPPM, DPPE and DPPP protected Ag_{29} , respectively). The lifetime values for longer chain length phosphines are in the microsecond (μs) range and also these clusters show PL quenching in the presence of O_2 . Both these observations imply that the PL originates through a phosphorescence process. This process is also enhanced when

heavy ligands are introduced (such as TTP, TFPP and TCPP). A similar kind of PL enhancement is also observed in the case of $[Ag_{51}(BDT)_{19}(PPh_3)_3]^{3-}$ upon replacing PPh_3 with DPPM, DPPE and DPPP. Selective quenching upon O_2 exposure is used to develop a sensor.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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