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2024, 12, 685Host–guest complexes of perylene bisimide-based
metallacage and fullerenes for efficient
photoinduced charge separation†O. A. Stasyuk, ^a M. Solà ^{*a} and A. J. Stasyuk ^{*ab}

The discovery of coordination-driven self-assembly has greatly expanded the field of organic macrocyclic compounds. This approach enables the construction of precise supramolecular complexes, known as metallacages, assembled from organic ligands coordinated with metal centers. Metallacages come in various sizes and shapes, making them capable of hosting guest molecules of different sizes. In this work, we report the ground and excited state properties of non-covalent complexes between various fullerenes (C_{60} , C_{70} , $Sc_3N@C_{80}$, $Sc_3CH@C_{80}$, and $Sc_4O_3@C_{80}$) and Pt_6PBI_3 metallacage, composed of perylene bisimide units and organoplatinum nodes. These complexes exhibit thermodynamically favorable photoinduced charge transfer from endohedral metallofullerenes to metallacage that occurs within picoseconds. Among the systems considered, the $Pt_6PBI_3 \supset Sc_3N@C_{80}$ complex stands out as the most promising candidate for use in photovoltaics due to its ability for fast charge separation and slow charge recombination.

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Introduction

Organic macrocyclic compounds, such as crown ethers,¹ cryptands,² and cavitands^{3,4} became widespread and firmly established in the routine life of chemists almost immediately after their discovery.⁵ Due to their ability to engage in multiple non-covalent interactions and selectively bind small cationic species, they are widely used as phase transfer catalysts,^{6,7} specific metal cation sensors,^{8,9} or even as compounds that facilitate ion transport across cell membranes (ionophore) in biological applications.¹⁰ Cyclodextrins are another type of macrocyclic compound composed of glucopyranoside sugar molecules bound together in rings of various sizes. Depending on their size, they can accommodate neutral or charged molecules.¹¹ This ability, in combination with very low toxicity, allows cyclodextrins to find broad applications as drug delivery agents in numerous official approved medicines.^{12–14} However,

due to the narrow cavity size, their host–guest chemistry is limited to small molecules and often has restricted use in polar protogenic environments. Porous organic cages¹⁵ with shape-stable structures are of particular interest in supramolecular chemistry due to their internal cavities of different size and ability to bind to guest molecules, such as fullerenes.^{16–18} Charge-separated states with long lifetimes were observed in porphyrin-based organic cages with encapsulated C_{60}/C_{70} fullerenes.^{17,19}

The discovery of coordination-driven self-assembly has significantly expanded host–guest chemistry.^{20–22} This powerful tool allows for precise construction of supramolecular complexes, such as metal–organic cages or metallacages, in various shapes and sizes.^{23,24} Metal–organic cages are molecular assemblies of organic ligands coordinated with either metal cations or metal oxide clusters of different nuclearities, resulting in architectures with inherent porosity. Similar to other macrocyclic compounds, metal–organic cages are capable of binding various organic guests. At the same time, since the size and shape of metal–organic cages can vary broadly, the size of the guest molecule can also differ significantly.^{25,26}

Since the majority of metallacages are constructed from rigid organic fragments, enhancing non-covalent interactions is a natural approach to facilitate their hosting ability.^{27,28} Therefore, the ideal building blocks for preparation of metallacages with promising host–guest chemistry are extended π -conjugated organic ligands, such as polycyclic aromatic hydrocarbons,^{29–31} porphyrins,^{32–36} or rylene bisimides.^{37–40}

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† Electronic supplementary information (ESI) available: Supporting information is available and includes a detailed computational methodology, characteristics of interactions between fullerenes and metallacage (QTAIM, NCI, and energy decomposition data), charge separation values and rates of photoinduced electron transfer. Cartesian coordinates for all studied systems are also provided. See DOI: <https://doi.org/10.1039/d3tc03412g>

In 2013, Würthner and co-workers first synthesized and characterized a giant tetrahedral host (M_4L_6), assembled from octahedral Fe(II) ions and linear perylene bisimide (PBI) dyes with 2,2'-bipyridine groups.⁴¹ The reported cage, with an edge length of 3.9 nm and an estimated internal volume of more than 950 Å³, exhibits broad and strong absorption in the visible region (up to 650 nm). Moreover, it demonstrates a total of 7 highly reversible electrochemical oxidation and reduction waves. The ability to encapsulate C₆₀ fullerene was demonstrated through UV-Vis and NMR spectroscopy, as well as mass spectrometry. It is important to note that spectroscopic measurements suggest that each cage can accommodate two fullerenes. The evolution of this work led to the synthesis of a structurally similar metallacage in which Fe(II) ions were replaced by Zn(II) ions.⁴² This replacement dramatically enhanced the cage's fluorescence quantum yield. The new cage also demonstrates the ability to accommodate aromatic guests, coronene and perylene, with host-guest ratio of 1:2 and 1:3, respectively.

In 2020, Fang, Stang, and their co-workers reported a novel supramolecular complex constructed through the coordination-driven self-assembly of *o*-tetrapyridyl perylene bisimide with *cis*-(PtEt₃)₂Pt(OTf)₂.⁴³ The synthesized metallacage (**Pt₆PBI₃**) has the shape of a trigonal prism and possesses an inner cavity with a diameter of 14.7 Å. A cavity of this size is suitable for accommodating both C₆₀ and C₇₀ fullerenes, providing free rotation of the fullerenes inside it. However, as has been demonstrated, the cage exhibits a greater affinity towards C₇₀. This, combined with the possibility of fabricating monomolecular membranes, opens up broad application perspectives for **Pt₆PBI₃** and its host-guest complexes.

In this work, we report a theoretical study of the electronic and photophysical properties of the host-guest complexes of **Pt₆PBI₃** and various fullerenes. We conduct a comprehensive analysis of the photoinduced electron transfer (PET) occurring in the complexes by means of DFT/TDA-DFT method. The obtained results show that the **Pt₆PBI₃** metallacage exhibits a strong electron acceptor nature. The complexes formed with fullerene guests can exhibit either intense fluorescence or pronounced PET properties.

Computational methods

Geometry optimizations were performed utilizing the DFT BLYP^{44,45} exchange-correlation functional along with the empirical D3(BJ) dispersion correction^{46,47} and def2-SVP basis set.^{48,49} The calculations were performed within the ORCA 5.0.3 program.^{50,51} Energy decomposition analysis (EDA) at BLYP-D3(BJ)/TZP level was performed using the Amsterdam density functional (ADF) program.⁵² For electronic structure calculations and vertical excitation energies, the TDA formalism⁵³ with the range-separated CAM-B3LYP functional⁵⁴ and def2-SVP basis set^{48,49} was employed in Gaussian 16 (rev. A.03).⁵⁵ Population analysis was performed within Mulliken,⁵⁶ Löwdin,⁵⁷ Hirshfeld,⁵⁸ and CM5⁵⁹ schemes. Solvent effects were accounted

using a COSMO-like polarizable continuum model (C-PCM) with acetonitrile as a solvent (dielectric constant $\epsilon = 35.69$).^{60,61} Topological analysis of the electron density distribution was conducted using the "quantum theory of atoms in molecules" (QTAIM). Properties of electron density at the bond critical points (BCPs), such as electron density [$\rho(r)$], its Laplacian [$\nabla^2\rho(r)$], potential energy density [$V(r)$], kinetic energy density [$G(r)$], and total electron energy density [$H(r)$] were evaluated using the AIMALL suite.⁶² Chemcraft 1.8 program⁶³ was utilized for molecular structures and frontier molecular orbitals visualization. Further methodological details, including analysis of excited states, calculation of electron transfer rates, reorganization and interaction energies are available in the ESI.†

Results and discussion

Ground state properties of **Pt₆PBI₃** metallacage and its complexes with C₆₀/C₇₀ fullerenes

The encapsulation of C₆₀ and C₇₀ fullerenes in **Pt₆PBI₃** metallacage was experimentally carried out in acetone solution and robustly confirmed by a combination of multinuclear NMR and mass-spectrometry.⁴³ A series of NMR measurements taken over an extended period of time for a very dilute solution of **Pt₆PBI₃**⊃C₆₀ and **Pt₆PBI₃**⊃C₇₀ complexes revealed no indication of complex instability. The electronic complementarity between the metallacage and fullerenes, along with their ability to undergo reversible electrochemical oxidation/reduction suggests strong electronic communication between the units in both ground and excited states. However, cyclic voltammetry and spectroscopic studies indicated that fullerene encapsulation has only a limited effect on the electronic nature of the metallacage, suggesting weak electronic communication between the host and guest units.

To gain deeper insights into the behavior of the **Pt₆PBI₃** metallacage and the fullerenes in their free state and within the corresponding host-guest complexes, a detailed comparison of their electronic properties was conducted. The optimized ground state (GS) geometries of the **Pt₆PBI₃**⊃C₆₀ and **Pt₆PBI₃**⊃C₇₀ complexes are shown in Fig. 1.

It is well known that fullerenes possess strong electron-acceptor properties. As depicted in Fig. 1, the lowest unoccupied molecular orbital (LUMO) of the metallacage is almost 1 eV lower in energy than LUMO of C₆₀/C₇₀, indicating its exceptionally strong electron-acceptor capabilities. In the **Pt₆PBI₃**⊃C₆₀ and **Pt₆PBI₃**⊃C₇₀ complexes, the LUMO remains localized on the cage, and its energy is nearly identical to that of the isolated metallacage. The nature of the highest occupied molecular orbital (HOMO) is somewhat different in the complexes with C₆₀ and C₇₀. In **Pt₆PBI₃**⊃C₆₀, the HOMO is delocalized over both host and guest units in a ratio of 0.64:0.36, respectively. Meanwhile, in **Pt₆PBI₃**⊃C₇₀, the degree of HOMO localization increases to a ratio of 0.88:0.12. Thus, the destabilization of the HOMO observed during the complex formation is attributed to its partial delocalization over the fullerene units. Given the strong electron-acceptor properties of the metallacage, we checked the charge



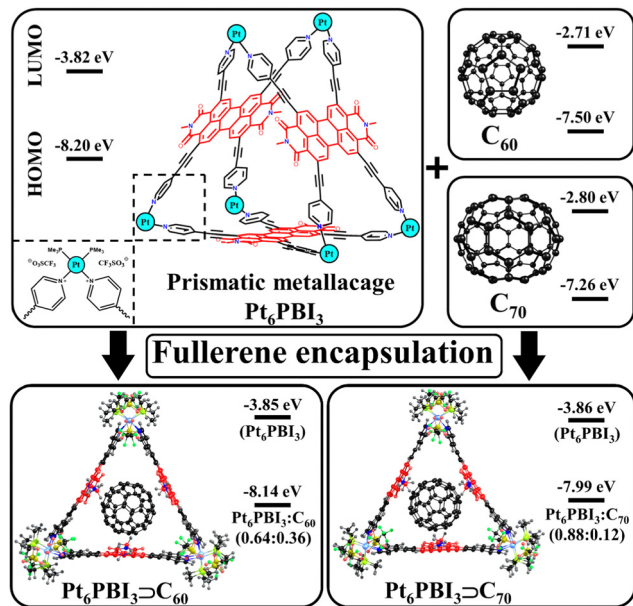


Fig. 1 Structure of $\text{Pt}_6\text{PBI}_3 \cdot \text{C}_{60}$ and $\text{Pt}_6\text{PBI}_3 \cdot \text{C}_{70}$ complexes. HOMO and LUMO energies of Pt_6PBI_3 , C_{60} , and C_{70} in free state and in the corresponding complexes.

separation between host and guest units in the GS. However, population analysis performed within commonly used schemes did not reveal any significant charge transfer between the units, charge separation in GS does not exceed 0.1 e (Table S1, ESI†). Thus, the slight differences in orbital energies observed upon complexation, coupled with the absence of GS charge separation, validate the limited electronic communication between the metallacage and fullerenes, which has been previously observed in the electrochemical and spectroscopic studies.⁴³

To assess the stability of the complexes, we calculated the interaction energy (ΔE_{int}) between the Pt_6PBI_3 cage and $\text{C}_{60}/\text{C}_{70}$ fullerenes, as well as the deformation energy (ΔE_{def}) associated with the distortion of the units from their equilibrium geometries to the geometries they adopt in the complexes. For $\text{Pt}_6\text{PBI}_3 \cdot \text{C}_{60}$ and $\text{Pt}_6\text{PBI}_3 \cdot \text{C}_{70}$, ΔE_{int} is -61.5 and -78.3 kcal mol⁻¹, while ΔE_{def} is 5.4 and 9.8 kcal mol⁻¹, respectively. The most of the deformation energy is attributed to the cage deformation, with deformation of the fullerenes contributing less than 10%. To analyze the nature of the host-guest interactions, we employed the Morokuma-like interaction energy decomposition analysis⁶⁴ implemented in the ADF program.⁵² The EDA decomposes the interaction energy into four components: electrostatic (ΔE_{elstat}), Pauli repulsion (ΔE_{Pauli}), orbital interactions (ΔE_{oi}), and dispersion correction (ΔE_{disp}). This decomposition enables us to assess the role of the specific interactions in the systems.

Table 1 represents the EDA analysis results showing similar nature of host-guest interactions in the complexes. Dispersion dominates (63%), followed by electrostatic attraction (24–25%), and orbital interactions (12–13%). The destabilizing term (ΔE_{Pauli}) is 92.6 for $\text{Pt}_6\text{PBI}_3 \cdot \text{C}_{60}$ and 112.5 kcal mol⁻¹ for $\text{Pt}_6\text{PBI}_3 \cdot \text{C}_{70}$. The complex with C_{70} also has higher deformation

energy compared to $\text{Pt}_6\text{PBI}_3 \cdot \text{C}_{60}$. Overall, based on the complexation energy values, $\text{Pt}_6\text{PBI}_3 \cdot \text{C}_{70}$ complex is more stable than $\text{Pt}_6\text{PBI}_3 \cdot \text{C}_{60}$, confirming the greater cage affinity to C_{70} observed in the experiment.⁴³

We used QTAIM calculations⁶⁵ to analyze the host-guest interaction topology in the $\text{Pt}_6\text{PBI}_3 \cdot \text{C}_{60}$ and $\text{Pt}_6\text{PBI}_3 \cdot \text{C}_{70}$ complexes, considering various topological parameters at BCPs (Table S2, ESI†). Numerical values of these parameters can provide information on the nature of interactions.⁶⁶ In both complexes, the analysis revealed only one type of interactions: C···C contacts between fullerene and host cage linkers. These interactions can be described as weak, closed-shell non-covalent interactions. Considering the π -conjugated nature of the guest and PBI units, the C···C contacts can be attributed to $\pi \cdots \pi$ interactions. No interactions of fullerenes with other metallacage parts were observed due to their spatial separation. In $\text{Pt}_6\text{PBI}_3 \cdot \text{C}_{60}$, 11 BCPs for $\pi \cdots \pi$ interactions were detected, while replacing C_{60} with C_{70} increases the number of BCPs to 15 in $\text{Pt}_6\text{PBI}_3 \cdot \text{C}_{70}$. QTAIM molecular graphs for both complexes are depicted in Fig. S1, ESI†. Considering the similar electron density characteristics at BCPs in both complexes but the higher number of BCPs in $\text{Pt}_6\text{PBI}_3 \cdot \text{C}_{70}$, the results correlate well with its stronger interaction energy. The non-covalent interaction (NCI) index analysis⁶⁷ showed qualitatively similar NCI isosurface arrangements in both complexes, resembling the metallacage shape. In particular, three distinct areas between PBI linkers and fullerene were observed. The reduced density gradient (RDG) plots and NCI isosurfaces are presented in Fig. S2 and S3, ESI†.

Singlet excited states of $\text{Pt}_6\text{PBI}_3 \cdot \text{C}_{60}$ and $\text{Pt}_6\text{PBI}_3 \cdot \text{C}_{70}$ complexes

Our results revealed relatively low LUMO energy for both the Pt_6PBI_3 cage and $\text{C}_{60}/\text{C}_{70}$ fullerenes: -3.82 and $-2.71/-2.80$ eV, respectively (Fig. 1). A very low-lying LUMO of Pt_6PBI_3 suggests its potential as a strong electron acceptor, capable of oxidizing fullerene under photoexcitation. However, study by Fang, Stang, and co-workers indicates only marginal changes in the UV-Vis spectrum of the cage upon fullerene inclusion.⁴³ To get deeper understanding of the processes taking place under photoexcitation, we performed simulations of excited states using the TDA-DFT method at the CAM-B3LYP-D3(BJ)/def2-SVP//BLYP-D3(BJ)/def2-SVP level of theory (see ESI† for computational details). The TDA-DFT performs well in reproducing experimental absorption and emission spectra of a series of medium-sized conjugated molecules⁶⁸ and is computationally feasible method for excited state simulations of large systems. Moreover, the range-separated CAM-B3LYP functional performs well for prediction of excitation energy and is particularly effective in modeling charge transfer processes in fullerene-based complexes, yielding a mean absolute percentage error of 6.3% for charge transfer rate values.⁶⁹

The complexes were split into two fragments: Pt_6PBI_3 and $\text{C}_{60}/\text{C}_{70}$ fullerene. We examined the electron density distribution for the 40 lowest singlet excited states. These states can be categorized into three types: (1) locally excited (LE) states, in



Table 1 EDA results (in kcal mol⁻¹) for **Pt₆PBI₃⊃C₆₀** and **Pt₆PBI₃⊃C₇₀** complexes at the BLYP-D3(BJ)/TZP level of theory^a

Complex	Energy terms					ΔE_{def}		$\Delta E_{\text{complex}}$
	ΔE_{Pauli}	ΔE_{elstat}	ΔE_{oi}	ΔE_{disp}	ΔE_{int}	Cage	Fullerene	
Pt₆PBI₃⊃C₆₀	92.57	-37.17 (24%)	-19.88 (13%)	-97.04 (63%)	-61.52	5.14	0.56	-56.10
Pt₆PBI₃⊃C₇₀	112.52	-47.15 (25%)	-23.39 (12%)	-120.27 (63%)	-78.29	9.41	0.40	-68.48

^a Relative values (in parentheses) are given as a percentage and express the contribution to the sum of all attractive energy terms: $\Delta E_{\text{elstat}} + \Delta E_{\text{oi}} + \Delta E_{\text{disp}}$. Complexation energy: $\Delta E_{\text{complex}} = \Delta E_{\text{int}} + \Delta E_{\text{def}}$.

which the exciton is mostly localized on either fullerene (LE^{Guest}) or **Pt₆PBI₃** (LE^{Host}) with charge separation (CS) below 0.1 *e*; (2) charge transfer (CT) states with significant charge separation (CS > 0.8 *e*); and (3) mixed states, involving both LE and CT contributions (0.1 *e* < CS < 0.8 *e*).

The gas-phase energies of the 40 lowest-lying singlet excited states of **Pt₆PBI₃⊃C₆₀** range from 2.50 to 3.28 eV. The first excited state, at 2.50 eV, corresponds to the LE^{Guest} state with exciton localization on C₆₀ (Table 2). The LE^{Host} state was found at 2.73 eV, *i.e.* 0.23 eV higher in energy compared to LE^{Guest}. The lowest CT state with 0.81 *e* transferred lies at 2.98 eV and can be described as [Pt₆PBI₃]⁻⊃[C₆₀]⁺. In the case of **Pt₆PBI₃⊃C₇₀**, the first 40 excited states have the energy range from 2.29 to 3.14 eV. The lowest-lying excited state, at 2.29 eV, is the LE^{Guest} state. The energy of the LE^{Host} state is very similar to that in **Pt₆PBI₃⊃C₆₀** and equal to 2.71 eV. Since the HOMO energy of C₇₀ is slightly higher than that of C₆₀, this fullerene should have a slightly improved electron-donor capability. Indeed, the energy of the CT state is 2.63 eV, which is 0.35 eV lower compared to the CT state in the complex with C₆₀. Similar to **Pt₆PBI₃⊃C₆₀**, this state results from an electron transfer from C₇₀ fullerene to the metallacage.

To understand how polar environment affects electronic excitations, we used a COSMO-like model^{60,61,70–72} with acetonitrile solvent. For the **Pt₆PBI₃⊃C₆₀** and **Pt₆PBI₃⊃C₇₀** complexes, GS dipole moments are 0.87 and 2.11 D, respectively. Their rather small values are due to symmetric structure of the metallacage and fullerene fragments. With Pt(II) centers, *o*-tetrapyrrolyl PBI and triflate counterions, both complexes are expected to have high solvation energies in the GS. In particular, their solvation energies are similar and equal to -5.29 and -5.28 eV. The change in the dipole moment ($\Delta\mu$) due to GS → LE^{Guest}/LE^{Host} excitations is small and hardly exceeds 1 D, keeping the solvation energies in both LE^{Guest} and LE^{Host} states similar to those in the GS. Solvation data for both complexes are given in Table S3, ESI†. The dipole moment changes from GS to CT states are usually much larger than those to LE states due to charge separation. In our study, **Pt₆PBI₃⊃C₆₀** and **Pt₆PBI₃⊃C₇₀** showed relatively small changes, namely 11.84 and 14.47 D, due to high symmetry and efficient charge delocalization. Solvation of the complexes stabilizes CT states, lowering their energies from 2.96 to 2.68 eV and from 2.63 to 2.31 eV for **Pt₆PBI₃⊃C₆₀** and **Pt₆PBI₃⊃C₇₀**, respectively.

Table 2 Excitation energies (*E_x*, eV), main singly excited configuration (HOMO(H)–LUMO(L)) with the largest squared coefficient in the configuration–interaction (CI coef.), oscillator strength (*f*), extent of charge transfer (CT, *e*) or localization of exciton (*X*) computed for **Pt₆PBI₃⊃C₆₀** and **Pt₆PBI₃⊃C₇₀** complexes in the gas-phase (VAC) and acetonitrile (ACN)

	Supramolecular system			
	Pt₆PBI₃⊃C₆₀		Pt₆PBI₃⊃C₇₀	
	VAC	ACN	VAC	ACN
LE ^{Guest} (C ₆₀ /C ₇₀)				
<i>E_x</i>	2.500	2.499	2.289	2.284
Transition (CI coef.)	H–2–L+3 (0.20)	H–1–L+4 (0.24)	H–L+3 (0.45)	H–L+3 (0.48)
<i>f</i>	<0.001	0.001	<0.001	<0.001
<i>X</i>	0.922	0.902	0.930	0.908
LE ^{Host} (Pt ₆ PBI ₃)				
<i>E_x</i>	2.727	2.698	2.711	2.678
Transition (CI coef.)	H–8–L (0.13)	H–5–L+2 (0.20)	H–3–L+2 (0.14)	H–3–L+1 (0.25)
<i>f</i>	0.015	0.027	0.205	0.207
<i>X</i>	0.865	0.868	0.888	0.885
Most intense absorption band				
<i>E_x</i>	2.792	2.741	2.789 ^a	2.739
Transition (CI coef.)	H–L+2 (0.28)	H–5–L+1 (0.27)	H–6–L+5 (0.05)	H–5–L (0.23)
<i>f</i>	1.787	2.199	1.266	1.193
Localization	Pt₆PBI₃	Pt₆PBI₃	Pt₆PBI₃	Pt₆PBI₃
<i>X</i>	0.887	0.860	0.754	0.833
CT (C ₆₀ /C ₇₀ → Pt ₆ PBI ₃)				
<i>E_x</i>	2.982	2.678	2.632	2.305
Transition (CI coef.)	H–2–L+2 (0.17)	H–4–L+2 (0.21)	H–2–L+2 (0.23)	H–1–L+1 (0.47)
<i>f</i>	0.030	0.027	0.009	0.006
CT	0.813	0.885	0.858	0.928

^a Mixed state with significant contributions of both LE and CT.

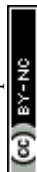


Table 3 Gibbs energy (ΔG^0 , in eV), electronic coupling ($|V_{ij}|$, in eV), reorganization energy (λ , in eV), Huang–Rhys factor (S_{eff}), rates (k_x , in s^{-1}) and characteristic time (τ , in ns) for CS and CR processes in $\text{Pt}_6\text{PBI}_3 \supset \text{C}_{60}$ and $\text{Pt}_6\text{PBI}_3 \supset \text{C}_{70}$ complexes in ACN

Complex $\text{Pt}_6\text{PBI}_3 \supset \text{C}_{\text{xx}}$	Transition	ΔG^0 ^a	$ V_{ij} $	λ	S_{eff} ^b	k_x	τ
$\text{Pt}_6\text{PBI}_3 \supset \text{C}_{60}$	$\text{LE}^{\text{Guest}} \rightarrow \text{CT}$	0.179	2.34×10^{-3}	0.744	1.26	4.95×10^6	202.1
	$\text{CT} \rightarrow \text{GS}$	−2.678	2.87×10^{-2}	0.724	1.15	7.32×10^6	136.6
$\text{Pt}_6\text{PBI}_3 \supset \text{C}_{70}$	$\text{LE}^{\text{Guest}} \rightarrow \text{CT}$	0.021	2.42×10^{-3}	0.683	1.12	3.54×10^8	2.8
	$\text{CT} \rightarrow \text{GS}$	−2.305	1.24×10^{-2}	0.680	1.10	3.23×10^7	31.0

^a Gibbs energy difference between the given states. ^b Effective value of the Huang–Rhys factor $S_{\text{eff}} = \lambda_i / \hbar \omega_{\text{eff}}$, where $\hbar \omega_{\text{eff}}$ is set to 1600 cm^{-1} .

Thus, stabilization of the CT states significantly reduces the energy gap between the CT and the lowest excited state (LE^{Guest}), making CT population possible from this state.

The method of Ulstrup and Jortner^{73,74} was employed to estimate charge separation (k_{CS}) and charge recombination (k_{CR}) rates using four parameters, such as electronic coupling of initial and final states (V_{ij}), solvation reorganization energy (λ_s), reaction Gibbs energy (ΔG^0), and Huang–Rhys factor (S_{eff}). We used an effective frequency of 1600 cm^{-1} , corresponding to C=C bond stretching. Testing the effect of the selected frequency on the rate did not reveal significant changes (Table S4, ESI†). The k_{CS} and k_{CR} rates calculated in ACN are listed in Table 3.

In Table 3, $\text{Pt}_6\text{PBI}_3 \supset \text{C}_{60}$ complex shows charge separation with positive Gibbs energy, taking place in the inverted Marcus region ($|\Delta G^0| > \lambda$). The rate of this process is $4.95 \times 10^6 \text{ s}^{-1}$. At the same time, charge recombination ($\text{CT} \rightarrow \text{GS}$) occurs in a deep inverted Marcus region ($|\Delta G^0| \gg \lambda$). The rates for CS and CR differ by less than two times, with CR surpassing CS. The predicted $k_{\text{CS}}/k_{\text{CR}}$ ratio suggests that the CT state formation is unlikely in $\text{Pt}_6\text{PBI}_3 \supset \text{C}_{60}$. In turn, $\text{Pt}_6\text{PBI}_3 \supset \text{C}_{70}$ has near-zero Gibbs energy for CS, therefore this process is more thermodynamically favorable than in $\text{Pt}_6\text{PBI}_3 \supset \text{C}_{60}$. The CS and CR rates for $\text{Pt}_6\text{PBI}_3 \supset \text{C}_{70}$ are significantly faster compared to $\text{Pt}_6\text{PBI}_3 \supset \text{C}_{60}$, the processes occur in nanoseconds (2.8 ns for CS and 31.0 ns for CR). The slower CR than CS implies a detectable CT state lifetime, although formation of the CT state has not been observed in UV-Vis experiment.⁴³ The fluorescence measurements for empty metallacage and both complexes with fullerenes show minimal difference in fluorescence decay. The amplitude weighted average fluorescence lifetimes are 2.42, 2.56, and 2.71 ns for Pt_6PBI_3 , $\text{Pt}_6\text{PBI}_3 \supset \text{C}_{60}$, and $\text{Pt}_6\text{PBI}_3 \supset \text{C}_{70}$, respectively. Thus, radiative deactivation of excited state is much faster than CT state generation for $\text{Pt}_6\text{PBI}_3 \supset \text{C}_{60}$ (2.6 ns vs. 202.1 ns) and comparable for $\text{Pt}_6\text{PBI}_3 \supset \text{C}_{70}$ (2.7 ns vs. 2.8 ns).

Hence, the absence of experimental detection of the CT state in the studied complexes results from faster radiative deactivation (fluorescence) than CT state formation. Notably, in $\text{Pt}_6\text{PBI}_3 \supset \text{C}_{60}$, the formation of the CT state is also slower than non-radiative charge recombination. Fig. 2 highlights the fluorescence and charge transfer processes following photoexcitation of the $\text{Pt}_6\text{PBI}_3 \supset \text{C}_{60}$ and $\text{Pt}_6\text{PBI}_3 \supset \text{C}_{70}$.

Facilitating electron transfer using endohedral metallofullerenes

It is known that an increase in the size of fullerene leads to an increase in its donor abilities. A comparison of the HOMO and

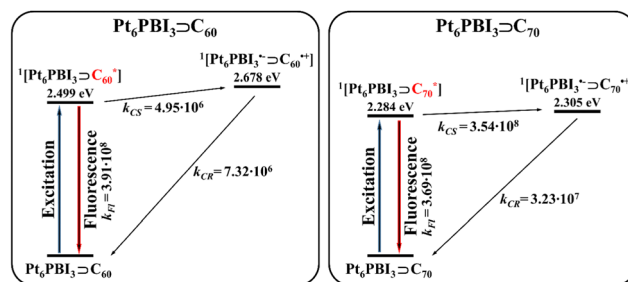


Fig. 2 Summary of the excited state processes for $\text{Pt}_6\text{PBI}_3 \supset \text{C}_{60}$ and $\text{Pt}_6\text{PBI}_3 \supset \text{C}_{70}$ in ACN. Fluorescence rates are taken from ref. 43.

LUMO energies of pristine C_{60} , C_{70} , and C_{84} fullerenes (Fig. 3) clearly demonstrates an increase in their HOMO energy from -7.50 eV for C_{60} to -7.08 eV for C_{84} . The observations made based on the HOMO energy are in a good agreement with the experimentally measured ionization energies of fullerenes, which are equal to 7.57, 7.36, and 7.17 eV for C_{60} , C_{70} , and C_{84} , respectively.⁷⁵

As the electron-acceptor properties of Pt_6PBI_3 proved insufficient to withdraw electron from C_{60} and C_{70} fullerenes, we hypothesized that replacing these pristine fullerenes with more effective electron donors could facilitate charge transfer. Earlier, we demonstrated that metal nitride endohedral fullerenes effectively donate electrons in complexes with carbon-rich acceptors, such as pristine fullerenes and γ -graphynes.^{76,77} Guided by these results, we aimed to evaluate the feasibility of the PET in a series of complexes composed of the Pt_6PBI_3 metallacage and various endohedral $\text{I}_h\text{-C}_{80}$ -based metallofullerenes. As it can be seen in Fig. 3, the HOMO energies of endohedral

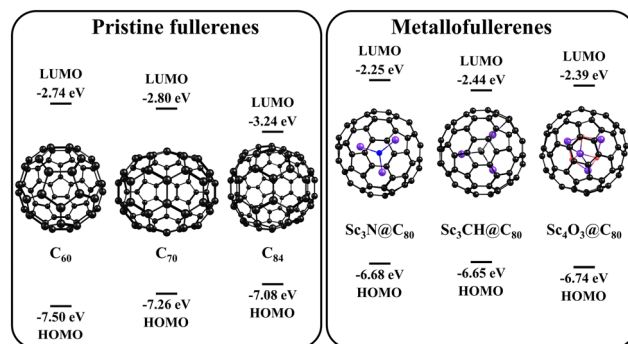
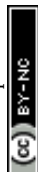


Fig. 3 HOMO and LUMO energies (in eV) of pristine and endohedral metallofullerenes.



metallofullerenes are higher compared to those of the pristine fullerenes of a similar size, suggesting better donor properties, even surpassing those of C_{84} fullerene. This change can be explained by a partial charge transfer between the metal cluster and fullerene cage, thus the electronic structure of the considered metallofullerenes $M@C_{80}$ can be represented as $M^{\delta+}@C_{80}^{\delta-}$. Importantly, the host size is suitable to accommodate these metallofullerenes, given their diameter is only 20% larger than that of C_{60} . As cluster-encapsulated fullerenes, we selected three experimentally obtained systems: scandium nitride ($Sc_3N@C_{80}$),⁷⁸ hydrogenated scandium carbide ($Sc_3CH@C_{80}$),^{79,80} and scandium oxide ($Sc_4O_3@C_{80}$)⁸¹ endohedral fullerenes (Fig. 3). The structures of $Pt_6PBI_3 \supset Sc_3N@C_{80}$, $Pt_6PBI_3 \supset Sc_3CH@C_{80}$, and $Pt_6PBI_3 \supset Sc_4O_3@C_{80}$ were optimized using the BLYP-D3(BJ) functional and def2-SVP basis set.

Given that the metallofullerenes are larger than C_{60} and C_{70} , we first checked the stability of the new complexes. The analysis performed according to the same scheme as for $Pt_6PBI_3 \supset C_{60}$ and $Pt_6PBI_3 \supset C_{70}$ revealed some interesting features of these systems. First, the deformation energy of new complexes is noticeably higher than that of complexes with pristine fullerenes. At the same time, the main contribution to the deformation energy is made by the deformation of metallacage, as in the C_{60} and C_{70} based complexes. Second, the interaction energies are higher compared to $Pt_6PBI_3 \supset C_{60}$ and $Pt_6PBI_3 \supset C_{70}$ due to the larger dispersion correction term. Overall, the complexation energies range from -63.9 to -67.8 kcal mol⁻¹ (Table S5, ESI†). Note that the nature of the interactions in all studied complexes is very similar. Thus, the stability of the new complexes is in between of the energy range for $Pt_6PBI_3 \supset C_{60}$ and $Pt_6PBI_3 \supset C_{70}$. Therefore, the binding affinity of the metallacage to the studied fullerenes is in the following order: $C_{70} > Sc_4O_3@C_{80} > Sc_3N@C_{80} > Sc_3CH@C_{80} > C_{60}$. Since the complexes with pristine fullerenes were successfully synthesized and isolated, we are convinced that the synthesis of the proposed complexes with metallofullerenes is also possible.

Fig. 4 shows that LUMO in all cases is located on one of the PBI subunits of the metallacage. Its energy is almost equal to the LUMO energy in $Pt_6PBI_3 \supset C_{60}$ and $Pt_6PBI_3 \supset C_{70}$. In turn, due to the better electron-donor ability of the endohedral metallofullerenes, the HOMO energy in their complexes is in between -7.39 and -7.49 eV, which is higher than the HOMO energies predicted for the complexes with pristine fullerenes (-8.14 and -7.99 eV for $Pt_6PBI_3 \supset C_{60}$ and $Pt_6PBI_3 \supset C_{70}$). In addition, the HOMO in the metallofullerene-based complexes is fully localized on the fullerene, unlike the originally described complexes with pristine fullerenes (Fig. 1). The mentioned differences should facilitate the photoinduced electron transfer in the new systems. To test this assumption, we analyzed the electron density distribution for their 40 lowest singlet excited states.

In all cases, the energies of the excited states in the gas-phase vary from 2.1 to 3.1 eV. The LE state energies of both LE^{Guest} and LE^{Host} turned out to be similar. The CT state in the complexes of interest is characterized by energies from 2.15 to 2.35 eV, depending on the particular complex. It is much lower

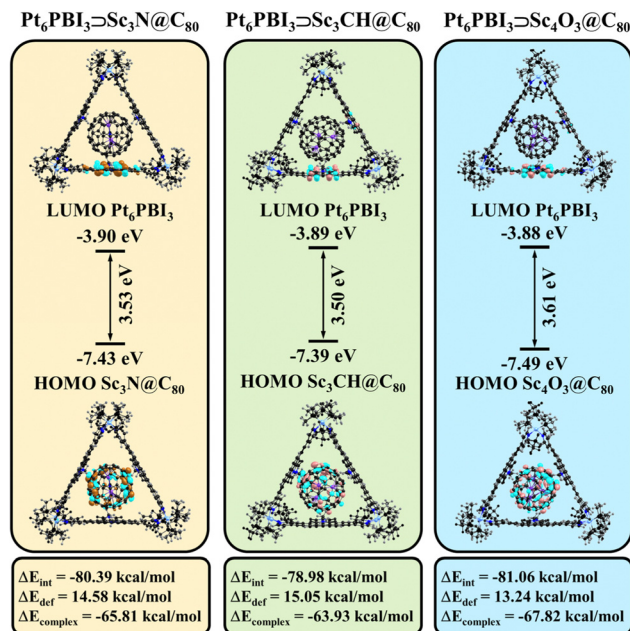
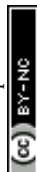


Fig. 4 Structure and HOMO/LUMO energies (in eV) of $Pt_6PBI_3 \supset Sc_3N@C_{80}$, $Pt_6PBI_3 \supset Sc_3CH@C_{80}$, and $Pt_6PBI_3 \supset Sc_4O_3@C_{80}$ complexes.

than the CT state energies in $Pt_6PBI_3 \supset C_{60}$ and $Pt_6PBI_3 \supset C_{70}$ (Table 4). Usually, the energies of the CT states correlate well with the HOMO–LUMO energy gap. It is important to note that for the $Pt_6PBI_3 \supset Sc_3CH@C_{80}$ complex, the CT state is the lowest excited state, even in the gas-phase. For other complexes, the energy difference between the CT state and the lowest LE state, with the exciton localized on the fullerene, does not exceed 0.15 eV. The frontier MOs representing the LE and CT states for

Table 4 Excitation energies (E_x , eV), main singly excited configuration (HOMO(H)–LUMO(L)) with the largest squared coefficient in the configuration-interaction (CI coef.), oscillator strength (f), extent of charge transfer (CT, e) or localization of exciton (X) computed for $Pt_6PBI_3 \supset Sc_3N@C_{80}$, $Pt_6PBI_3 \supset Sc_3CH@C_{80}$, and $Pt_6PBI_3 \supset Sc_4O_3@C_{80}$ complexes in the gas-phase (VAC)

	Supramolecular system		
	$Pt_6PBI_3 \supset XXX@C_{80}$		
	$Sc_3N@C_{80}$	$Sc_3CH@C_{80}$	$Sc_4O_3@C_{80}$
$LE^{Guest} (XXX@C_{80})$			
E_x	2.116	2.215	2.235
Transition (CI coef.)	H–4–L+4 (0.77)	H–L+3 (0.86)	H–L+3 (0.37)
f	0.013	<0.001	<0.005
X	0.923	0.920	0.886
$LE^{Host} (Pt_6PBI_3)$			
E_x	2.812	2.747	2.756
Transition (CI coef.)	H–13–L+3 (0.25)	H–7–L ()	H–5–L+2 (0.37)
f	0.446	0.439	0.431
X	0.872	0.881	0.889
CT ($XXX@C_{80} \rightarrow Pt_6PBI_3$)			
E_x	2.260	2.152	2.347
Transition (CI coef.)	H–4–L (0.40)	H–L+2 (0.74)	H–1–L (0.55)
f	0.014	0.013	0.010
CT	0.894	0.883	0.834



the $\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_3\text{N@C}_{80}$, $\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_3\text{CH@C}_{80}$, and $\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_4\text{O}_3\text{@C}_{80}$ complexes are shown in Fig. S4–S6, ESI†

The GS solvation energies of $\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_3\text{N@C}_{80}$, $\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_3\text{CH@C}_{80}$, and $\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_4\text{O}_3\text{@C}_{80}$ complexes turned out to be very close to those of the C_{60} and C_{70} based complexes and are equal to -4.83 , -5.18 , and -5.31 eV, respectively. The difference in dipole moments of the GS and both LE^{Guest} and LE^{Host} states is quite small and does not exceed 3.5 D. As expected, the solvation energies of these LE states are very similar to the solvation energies of GS. At the same time, the difference in dipole moments of GS and CT states in the complexes of interest is large: 10 D for $\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_3\text{N@C}_{80}$ and 21 D for $\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_3\text{CH@C}_{80}$ and $\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_4\text{O}_3\text{@C}_{80}$. Subsequently, the difference in solvation energies between GS and CT states is -0.34 eV for the complex with $\text{Sc}_3\text{N@C}_{80}$, and -0.58 and -0.54 eV for the complexes with $\text{Sc}_3\text{CH@C}_{80}$ and $\text{Sc}_4\text{O}_3\text{@C}_{80}$. Detailed solvation data in ACN are given in Table S6, ESI†. It is important to note that stabilization of the CT state is sufficient to reorder the LE^{Guest} and CT states in all complexes of interest. Fig. 5 shows the energies of the GS, LE, and CT states in the gas-phase and in ACN, as well as the simulated absorption spectra for all metallofullerene-based complexes.

The higher solvation energy of the CT states in $\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_3\text{CH@C}_{80}$ and $\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_4\text{O}_3\text{@C}_{80}$ compared to the $\text{Sc}_3\text{N@C}_{80}$ based complex can be explained by different charge delocalization over the host fragment measured by inverse participation ratio (IPR), which counts the number of atoms involved in the charge delocalization. For $\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_3\text{N@C}_{80}$, $\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_3\text{CH@C}_{80}$, and $\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_4\text{O}_3\text{@C}_{80}$, the calculated IPR values for the Pt_6PBI_3 host unit are 51.9 , 27.5 , and 28.4 (see Table S7 for details, ESI†). Charge delocalization over endohedral metallofullerene units is apparently less significant due to their lower accessibility to the solvent. The IPR value for the $\text{Sc}_3\text{N@C}_{80}$, $\text{Sc}_3\text{CH@C}_{80}$, and

$\text{Sc}_4\text{O}_3\text{@C}_{80}$ units are 30.4 , 20.0 , and 24.8 . Thus, higher charge delocalization and subsequently IPR values for both host and guest subunits in $\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_3\text{N@C}_{80}$ are responsible for its lower solvation in the CT state.

According to Table 4, GS $\rightarrow$ CT transitions in all complexes with metallofullerenes are characterized by a low oscillator strength, making direct population of the CT states through light absorption difficult. However, they can be generated by a decay of LE states. The k_{CS} and k_{CR} rates were calculated using the semi-classical approach.^{73,74} The main parameters used in calculation, as well as the rate values are given in Table 5.

Photoinduced electron transfer in the studied complexes is characterized by a negative Gibbs energy in the range from -0.19 to -0.60 eV. The estimated rates of CT generation are very high, thus the process occurs on a picosecond timescale. Characteristic time is 2 , 2 , and 1 ps, for $\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_3\text{N@C}_{80}$, $\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_3\text{CH@C}_{80}$, and $\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_4\text{O}_3\text{@C}_{80}$, respectively. The CR reaction proceeds in a deep inverted Marcus region ($|\Delta G^0| \gg \lambda$) and its rate varies considerably from complex to complex. In particular, for $\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_3\text{N@C}_{80}$, charge recombination is almost three orders of magnitude slower than the corresponding charge separation. At the same time, for $\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_3\text{CH@C}_{80}$, the charge recombination is only 14 times slower than charge separation. The $\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_4\text{O}_3\text{@C}_{80}$ complex is located in the middle, with a ratio of charge separation time to charge recombination time of approximately $1:150$. Considering the fact that PET depends not only on the rate of charge separation, but also on the efficiency of hole and electron extraction, the ideal combination for practical usage is characterized by fast charge separation and slow charge recombination. Therefore, it can be concluded that the $\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_3\text{N@C}_{80}$ complex is the best candidate among the considered systems for use as active layer in photovoltaic devices.

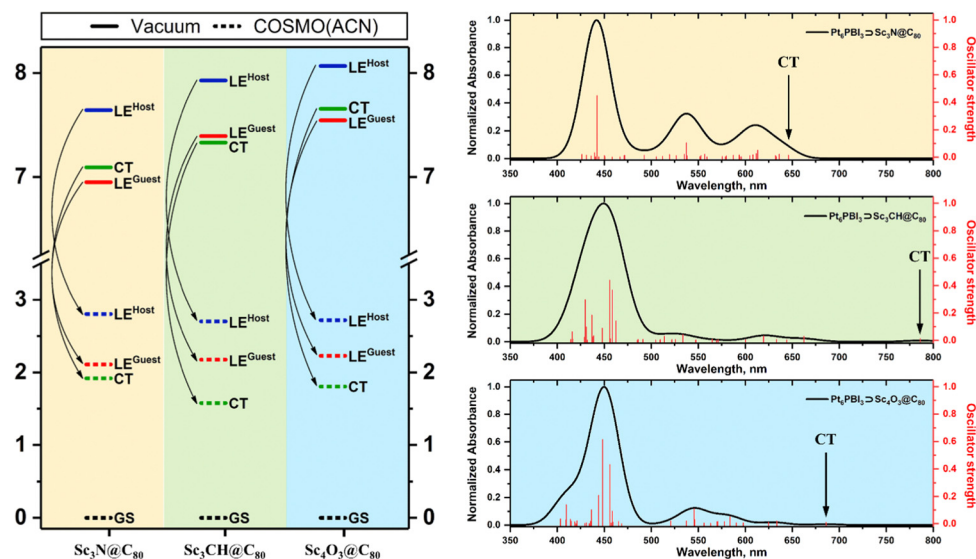


Fig. 5 (Left) Relative energies (in eV) of GS, LE, and CT states of $\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_3\text{N@C}_{80}$ (yellow), $\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_3\text{CH@C}_{80}$ (green), and $\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_4\text{O}_3\text{@C}_{80}$ (blue) complexes calculated in vacuum (VAC) and acetonitrile (ACN). (Right) Simulated absorption spectra of the studied complexes in ACN. The spectra were constructed using Gaussian broadening (FWHM = 0.15 eV). Red vertical lines show the oscillator strength for 40 lowest singlet excited states. Vertical arrows correspond to the positions of CT bands in the spectra.



Table 5 Gibbs energy ΔG^0 (in eV), electronic coupling $|V_{ij}|$ (in eV), reorganization energy λ (in eV), Huang–Rhys factor (S_{eff}), activation energy E_a (in eV), rates k_x (in s^{-1}) and characteristic time τ (in ps) for CS and CR processes in $\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_3\text{N@C}_{80}$, $\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_3\text{CH@C}_{80}$, and $\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_4\text{O}_3\text{@C}_{80}$ calculated in ACN

Complex $\text{Pt}_6\text{PBI}_3 \supset \text{C}_{xx}$	Transition	$\Delta G^0{}^a$	$ V_{ij} $	λ	$S_{\text{eff}}{}^b$	k_x	τ
$\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_3\text{N@C}_{80}$	$\text{LE}^{\text{Guest}} \rightarrow \text{CT}$	−0.191	5.83×10^{-3}	0.412	1.11	4.94×10^{11}	2
	$\text{CT} \rightarrow \text{GS}$	−1.920	5.25×10^{-2}	0.401	1.05	7.47×10^8	1339
$\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_3\text{CH@C}_{80}$	$\text{LE}^{\text{Guest}} \rightarrow \text{CT}$	−0.600	5.94×10^{-3}	0.534	1.02	4.95×10^{11}	2
	$\text{CT} \rightarrow \text{GS}$	−1.577	3.46×10^{-2}	0.531	1.00	3.60×10^{10}	28
$\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_4\text{O}_3\text{@C}_{80}$	$\text{LE}^{\text{Guest}} \rightarrow \text{CT}$	−0.422	8.85×10^{-3}	0.500	1.11	1.28×10^{11}	1
	$\text{CT} \rightarrow \text{GS}$	−1.807	5.26×10^{-2}	0.488	1.05	6.49×10^9	154

^a Gibbs energy difference between the given states. ^b Effective value of the Huang–Rhys factor $S_{\text{eff}} = \lambda_i/\hbar\omega_{\text{eff}}$, where $\hbar\omega_{\text{eff}}$ is set to 1600 cm^{-1} , which corresponds to the stretching of C=C bonds.

Conclusions

Using the DFT method, we showed that the Pt_6PBI_3 metallacage constructed from perylene bisimide units and organoplatinum nodes features an appropriately sized internal cavity, allowing it to form stable complexes not only with pristine C_{60} and C_{70} fullerenes but also with $\text{Sc}_3\text{N@C}_{80}$, $\text{Sc}_3\text{CH@C}_{80}$, and $\text{Sc}_4\text{O}_3\text{@C}_{80}$ metallofullerenes. Our calculations reveal that the binding affinities of the studied fullerenes to Pt_6PBI_3 follows this order: $\text{C}_{70} > \text{Sc}_4\text{O}_3\text{@C}_{80} > \text{Sc}_3\text{N@C}_{80} > \text{Sc}_3\text{CH@C}_{80} > \text{C}_{60}$.

The TDA-DFT results indicate that the metallacage has a lower LUMO energy than C_{60} and a high ability to delocalize an excess charge, ensuring its excellent electron-acceptor properties. However, the electron affinity of the metallacage is insufficient to withdraw an electron from C_{60} or C_{70} fullerenes. Charge separation in the $\text{Pt}_6\text{PBI}_3 \supset \text{C}_{60}$ and $\text{Pt}_6\text{PBI}_3 \supset \text{C}_{70}$ complexes is characterized by a small positive Gibbs energy and occurs within nanoseconds. Charge recombination is also fast in both complexes, serving as a competitive deactivation channel for the CT state. Moreover, the formation of the CT state in such complexes is hindered by the rapid radiative deactivation channel (fluorescence) of the corresponding LE states, which occurs more quickly than CT state formation.

However, replacing pristine fullerenes with metallofullerenes enables photoinduced electron transfer from fullerene to metallacage, a thermodynamically favorable process occurring within picoseconds. Importantly, in all cases, charge recombination is one to three orders of magnitude slower than the corresponding charge separation. Among the studied complexes, $\text{Pt}_6\text{PBI}_3 \supset \text{Sc}_3\text{N@C}_{80}$ demonstrates the best ratio of fast charge separation and relatively slow charge recombination, making it a highly promising candidate for photovoltaic systems.

Author contributions

O. A. S. investigation, formal analysis, writing – original draft, writing – review & editing. M. S. supervision, writing – review & editing, funding acquisition. A. J. S. investigation, supervision, writing – original draft, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

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