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Solvent dependent competition between fluorescence resonance energy transfer and through bond energy transfer in rhodamine appended hexaphenylbenzene derivatives for sensing of Hg^{2+} ions†

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Hexaphenylbenzene (HPB) derivatives **5** and **7** having rhodamine B moieties have been designed and synthesized, and have been shown to display solvent dependent. Fluorescence resonance energy transfer (FRET) and through bond energy transfer (TBET) in the presence of Hg^{2+} ions among the various cations (Cu^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, Ag^{+}, Ba^{2+}, Mg^{2+}, K^{+}, Na^{+}, and Li^{+}) have been tested. Derivative **5** displays quite high through bond energy transfer efficiency in the presence of Hg^{2+} ions in methanol whereas derivative **7** exhibits better FRET efficiency in the presence of Hg^{2+} ions in THF and CH_3CN than derivative **5**.

Introduction

Among various heavy metal ion pollutants, mercury contamination is widespread with distinct toxicological profiles. Mercury is found in different forms in many products like paints, electronic products and batteries, which enhance the severe effects on human health and environment.[1] Given these health and environmental concerns, efforts are being made for detection and quantification of Hg^{2+} ions in various environmental and biological samples. In this context, development of mercury selective fluorescent chemosensors[2] has attracted considerable research interest due to their high sensitivity, selectivity and simplicity over other traditional methods including atom absorption spectroscopy,[3] induced coupled plasma spectroscopy,[4] X-ray fluorescence spectrometry,[5] and anodic stripping voltammetry.[6] Several fluorescent chemosensors involving different photophysical processes like photoinduced electron/energy transfer,[7] metal–ligand charge transfer (MLCT),[8] intramolecular charge transfer (ICT),[9] excimer/exciplex formation,[10] imine isomerization,[11] chelation enhanced fluorescence (CHEF)[12] have been reported.

Recently, the labeling of organic molecules with fluorescent tags has attracted attention due to potential applications of such systems in biochemical experiments. Such systems have donors connected to acceptors *via* linkers and energy transfer (ET) in such systems occurs through space and through bonds.[13] The efficiency of FRET is controlled by the distance between the energy donor and energy acceptor fluorophores and the spectral overlap between the emission spectrum of the energy donor and the absorption spectrum of the energy acceptor,[14] whereas the TBET[15] systems are not limited by the constraint of such spectral overlap between the donor emission and the acceptor absorption. Furthermore, high energy transfer efficiencies, fast energy transfer rates and large pseudo-Stokes' shift enable applications of TBET systems as optical materials,[16] photosynthetic models,[17] in biotechnology[18] and as chemosensors. Recently, from our laboratory, we reported naphthalimide–rhodamine fluorescent dyad and pentaquinone–rhodamine dyad and triad which undergo TBET in the presence of Hg^{2+} ions in mixed aqueous media.[19] Now, in the present manuscript we have designed, synthesized and evaluated new rhodamine appended HPB derivatives in which the HPB unit acts as a donor and rhodamine as an acceptor. Synthesis of HPB derivatives has attracted great attention because of their potential applications in supramolecular and material chemistry.[20] HPB core has been used for the preparation of graphitic-like, dendritic and photoconductive polycyclic aromatic hydrocarbons or as a scaffold for a starlike array of functional materials such as porphyrin which have potential applications in the field of nanotechnology and molecular electronics. The unique propeller-shaped arrangement of six peripheral aryl groups around a central benzene ring in various HPB derivatives limit conjugation and disfavor extensive intermolecular π–π interactions. Keeping this in view, we designed and synthesized HPB-based derivatives **5** and **7** having rhodamine

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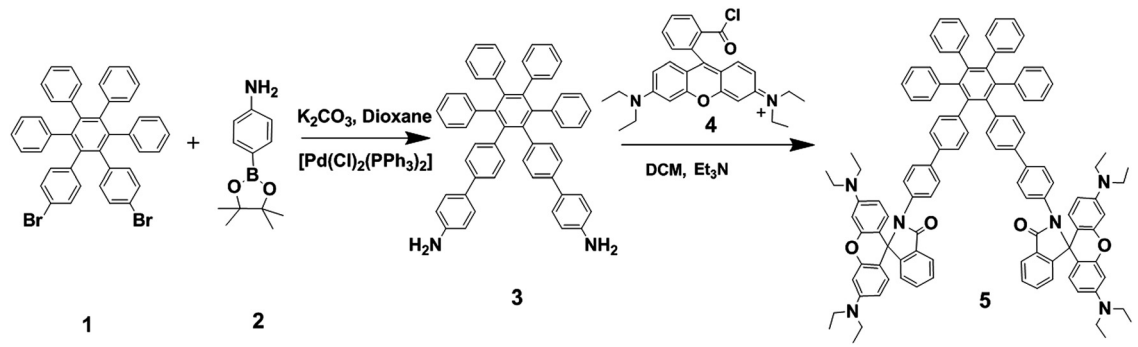
moieties. For a 'through bond energy transfer' process to come into effect there should be a low degree of conjugation between energy donor and energy acceptor and low degree of planarity. We envisioned that the HPB derivatives **5** and **7** having two/six rotors rotating around their own axis could impede the electron conjugation between donor and acceptor moieties thus, fulfilling the requirements for TBET to occur. Interestingly, derivatives **5** and **7** exhibit energy transfer by following both the mechanisms *i.e.* through space and through bond in the presence of Hg^{2+} ions and, interestingly, process of energy transfer is solvent dependent. To the best of our knowledge, this is the first report where donor–acceptor systems display solvent dependent switching of energy transfer mechanism in the presence of Hg^{2+} ions. In THF and CH_3CN through space energy transfer mechanism is operative whereas in protic solvent such as MeOH through bond energy transfer is operative.

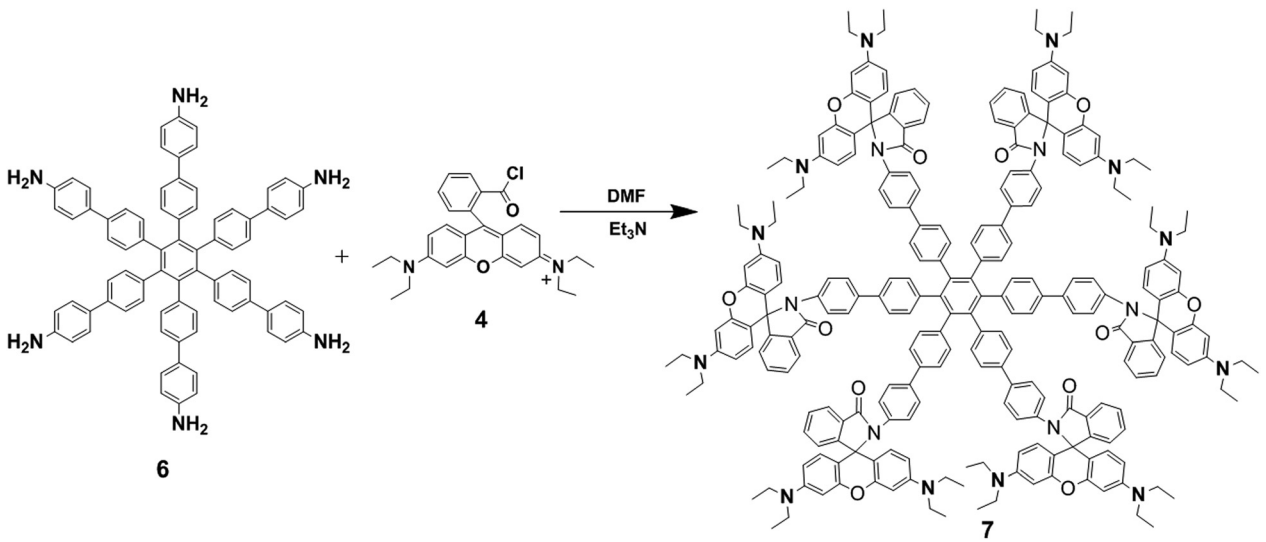
Results and discussion

The synthetic route for derivatives **5** and **7**, in which two and six rhodamine moieties are connected to the HPB core, respectively, each through a conjugated spacer is presented in Schemes 1 and 2, respectively. Suzuki–Miyaura cross coupling of compound **1** with boronic ester **2** furnished compound **3** in 53% yield. The ^{1}H NMR spectrum of compound **3** showed three doublets (4H each) and one multiplet (24H) corresponding to aryl protons (ESI, S3†). The mass spectrum of compound **3** showed parent ion peak at 717.4 corresponding to diamine **3** (ESI, S5†). A similar approach using a six-fold Suzuki–Miyaura coupling reaction of boronic ester **2** with hexakis(4-bromophenyl)benzene yielded derivative **6** in 70% yields.[21]

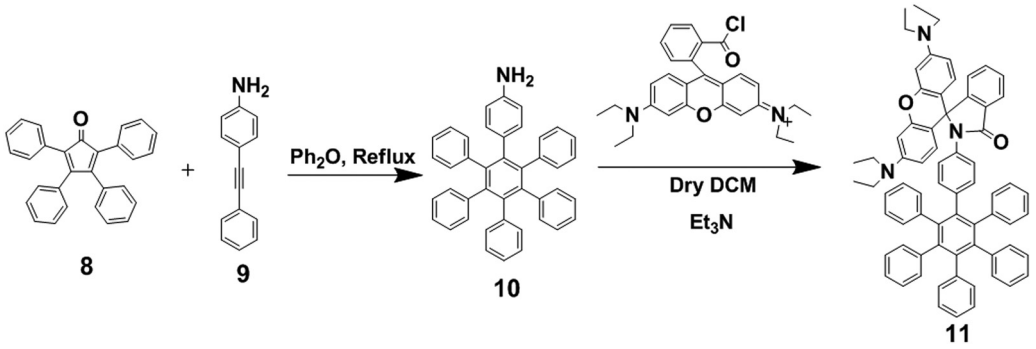
Furthermore, the reaction of derivatives **3** and **6** with rhodamine acid chloride **4**[22] in dichloromethane and *N*,*N*′-dimethylformamide furnished compounds **5** and **7** in 63% and 50% yields, respectively (Schemes 1 and 2). The structures of compounds **5** and **7** were corroborated from their spectroscopic and analytical data (ESI, S6–S11†). The ^{1}H NMR spectrum of compound **5** showed one triplet (24H), one quartet (16H), three doublets (4H, 2H, 2H), two multiplets (6H, 36H), and two broad signals (4H, 2H). The ^{1}H NMR spectrum of compound **7** showed one doublet (6H), five multiplets (72H, 48H, 18H, 18H and 18H) and two broad singlets (24H, 6H). The corresponding mass spectra showed parent ion peaks at



Scheme 1 Synthetic scheme of compound **5**.



Scheme 2 The synthetic scheme of compound **7**.



Scheme 3 The synthetic scheme of compound **11**.

1565.5 (M^+) and 3630.8 ($M + 1^+$) corresponding to the condensation products **5** and **7**, respectively. This spectroscopic data corroborates the structures of derivatives **5** and **7**. We also synthesized a model compound **11** in 44% yield in which one rhodamine unit is attached to HPB core without any spacer by reaction of rhodamine acid chloride **4** with compound **10** (Scheme 3) which was synthesized conveniently in 60% yield by Diels–Alder cycloaddition of tetraphenylcyclopentadienone **8** and compound **9**. The structures of compounds **10** and **11** were corroborated from their spectroscopic and analytical data (ESI, S12–S17†).

The binding behaviour of compounds **5** and **7** toward different cations (Cu^{2+}, Hg^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, Ag^+, Ba^{2+}, Mg^{2+}, K^+, Na^+, and Li^+) as their perchlorate salts was investigated by UV-Vis and fluorescence spectroscopy. The absorption spectrum of **5** (5 μM) exhibits two bands at 242 and 278 nm in THF (Fig. 1). The absence of any absorption transition at 400–600 region and appearance of colourless solution indicates lactonized conformation of rhodamine in the compound. However, upon addition of Hg^{2+} ions (0.1–20 equiv.), the intensity of absorption bands at 242 nm and 278 nm increased and a new band appeared at 554 nm (Fig. 1). These changes are accompanied by a gradual change of colour from colourless to pink, visible to the naked eye (inset, Fig. 1). The formation of a new band at 554 nm is attributed to the interaction of Hg^{2+} ions with the receptor **5** leading to the opening of spirolactam ring of rhodamine moiety to its ring opened amide conformation that facilitates the complexation. Thus, in the presence of mercury ions, compound **5** shows the absorption characteristics of both donor and acceptor components. No such observation was found in the presence of other metal ions except for Fe^{2+} where a slight colour change was observed on adding 20 equiv. of Fe^{2+} ions. Similar behaviour was observed in the case of compound **7** under the same experimental conditions as used for compound **5** (ESI, Fig. S1†). However, no variation in the absorption spectrum of derivative **7** was observed in the presence of other metal ions such as Cu^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, Ag^+, Ba^{2+}, Mg^{2+}, K^+, Na^+, and Li^+.

In the fluorescence spectrum, receptor **5** exhibited fluorescence emission at 506 nm in CH_3CN when excited at 290 nm which is attributed to the typical band of HPB moiety (Fig. 2). The rhodamine moiety in **5** remains in a closed, non-fluorescent spirolactam form indicating weak spectral overlap between hexaphenylbenzene (energy donor) emission and rhodamine (energy acceptor) absorption. As a result, the emission due to the HPB moiety is observed at 506 nm. In the presence of Hg^{2+} ions (50 equiv.), the emission band at 506 nm decreases along with the formation of new band characteristic of the acceptor component (rhodamine) at 585 nm (ϕ = 0.48) which is attributed to the opening of the spirolactam ring of rhodamine to an amide form (Scheme 4). Since the excitation wavelength of compound is 290 nm, a double frequency peak at 580 nm is anticipated which interferes with the emission

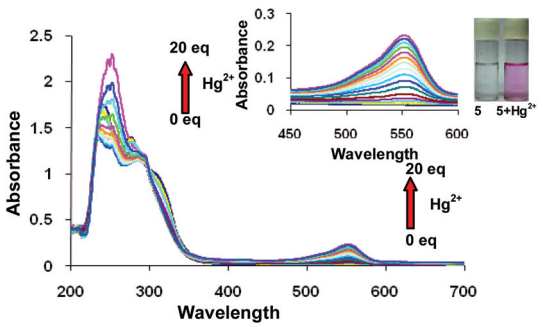


Fig. 1 UV-vis spectra of receptor **5** (5 μM) in the presence of Hg^{2+} ions (0–20 equiv.) in THF. Inset shows the change in color of **5** (5 μM) on addition of Hg^{2+} ions.

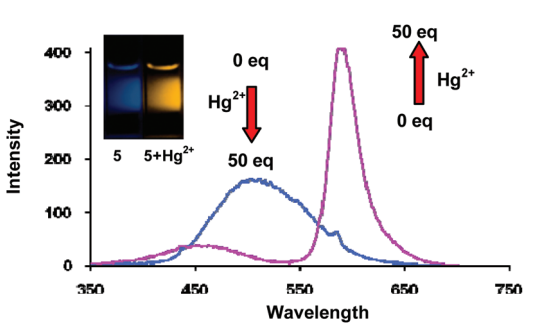
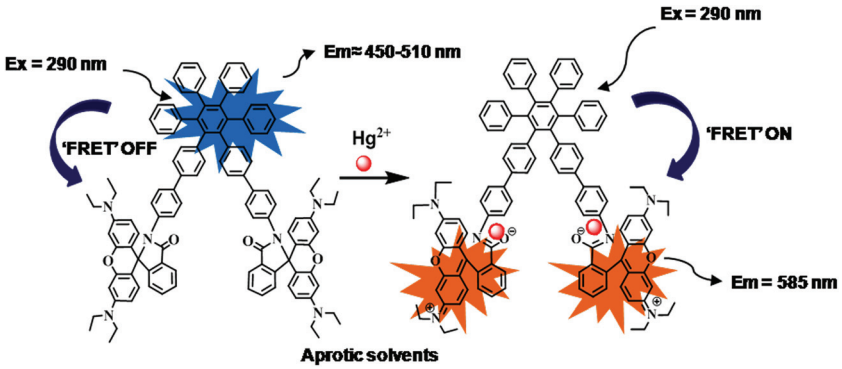


Fig. 2 Fluorescence response of receptor **5** (1 μM) on addition of Hg^{2+} (0–50 equiv.) in CH_3CN, λ_{ex} = 290 nm. Inset shows the change in the fluorescence on the addition of Hg^{2+} ions.



Scheme 4 Hg^{2+} induced FRET off–on in aprotic solvents.

band at 585 nm due to ring opened rhodamine moiety. The discrimination between rhodamine band and double frequency peak is done on the basis of the change in colour of fluorescence emission from blue to orange which indicates that the band at 585 nm is due to the spirolactam ring opening of rhodamine group (Fig. 2, inset). The emission spectrum of donor (HPB moiety) group and absorption spectrum of acceptor (rhodamine moiety) group show a spectral overlap (ESI, Fig. S4 and S5†) which results in fluorescence resonance energy transfer with large pseudo-stokes shift of 295 nm. Derivative **5** exhibits FRET efficiency of 67% and 10.8 folds of fluorescence enhancement at λ_{em} of 585 nm in acetonitrile. However in THF, compound **5** shows 7 fold fluorescence emission enhancement on addition of incremental amounts of Hg^{2+} ions (0.1–50 equiv.) with 43% FRET efficiency (ESI, Fig. S2†). Under the same experimental conditions as used for compound **5**, compound **7** (in CH_3CN) exhibits 12.9 fold fluorescence emission enhancement on addition of Hg^{2+} ions (0.1–50 equiv.) with 85% resonance energy transfer efficiency and 8.3 folds fluorescence emission enhancement in presence of Hg^{2+} ions (0.1–50 equiv.) with 60% resonance energy transfer efficiency in THF. These results suggest that the donor–acceptor systems **5** and **7** in the presence of Hg^{2+} ions undergo more emission enhancement and better resonance energy transfer efficiency in CH_3CN than that in THF (Table 1), thus, indicating possibility of solvent molecules playing the crucial role in metal–receptor complexation. We believe that CH_3CN being a coordinating solvent,[23] actively indulges in the complexation of Hg^{2+} ions with HPB derivatives **5** and **7** through solvent-assisted coordination apart from the receptors binding to the Hg^{2+} ions.

Interestingly, derivative **7** exhibits better FRET efficiency in THF (ESI, Fig. S3†) and in CH_3CN (Fig. 3) than that of derivative **5** as shown in Table 1. We propose that in derivative **7**, steric congestion caused by six rhodamine moieties restrict the rotation of the phenyl rings around their own axis and the conjugation across the donor and acceptor moieties is more facilitated, thus, through space energy transfer (FRET) is more facilitated in derivative **7** in comparison to derivative **5** where the steric congestion is relatively less.

To get more insight into role of solvent in metal–receptor complexation, we carried out the fluorescence studies of compound **5** and **7** in protic solvents such as MeOH, EtOH, *n*-PrOH and *n*-BuOH. On increasing the amounts of methanol in THF solution of compound **5**, the fluorescence of the compound **5** starts quenching with a considerable red shift (ESI, Fig. S6†) and is quenched completely in pure methanol. This

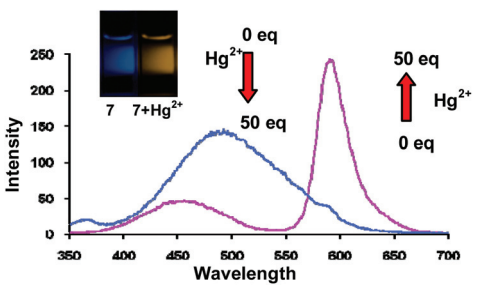


Fig. 3 Fluorescence response of receptor **7** (1 μM) on addition of Hg^{2+} (0–50 equiv.) in CH_3CN, λ_{ex} = 290 nm. Inset shows the change in fluorescence upon of Hg^{2+} ions.

Table 1 Comparison of fluorescence efficiency, quantum yields and fluorescence enhancement factor of **5** and **7**

	FRET								
	Acetonitrile			Tetrahydrofuran			TBET (methanol)		
Derivative	*E*	ϕ at λ = 585 nm	FEF	*E*	ϕ	FEF	*E*	ϕ at λ = 585 nm	FEF
5	0.67	0.02	10.8 fold	0.43	0.09	7 fold	0.98	4×10^{-3}	197 fold
5–Hg^{2+}		0.48			0.58			0.68	
7	0.85	0.012	12.9 fold	0.60	0.01	8.3 fold	0.92	3.4×10^{-3}	130 fold
7–Hg^{2+}		0.36			0.40			0.46	

E = efficiency, ϕ = quantum yield, FEF = fluorescence enhancement factor.

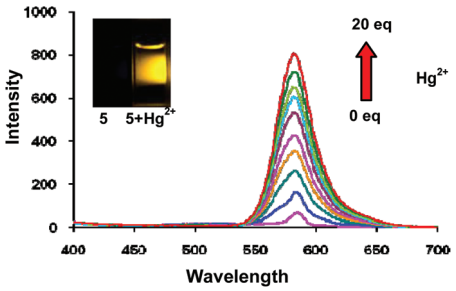
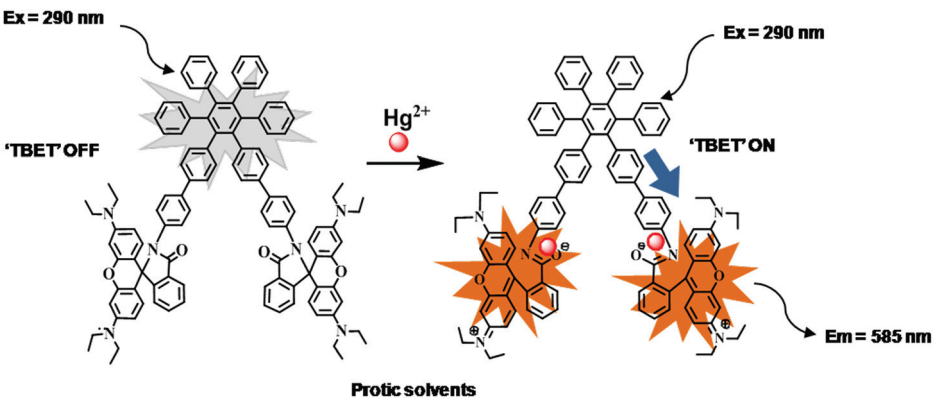


Fig. 4 Fluorescence response of receptor **5** (1 μM) on addition of Hg^{2+} (0.1–20 equiv.) in methanol, λ_{ex} = 290 nm. Inset shows the 'turned on' fluorescence of compound **5** on addition of Hg^{2+} ions.

quenching in fluorescence is due to the photoinduced electron transfer (PET) from nitrogen atom of the spirolactam ring to the photoexcited hexaphenylbenzene unit. Since, photoinduced electron transfer (PET) phenomenon is more operative in polar solvents than in non-polar solvents,[24] PET becomes more effective in methanol which leads to fluorescence quenching. On addition of incremental amounts of Hg^{2+} ions (0.1–20 equiv.) to the solution of receptor **5** in methanol, PET is blocked accompanied by the opening of spirolactam ring of rhodamine group which leads to the donor group (hexaphenylbenzene) to emit fluorescence energy which is rapidly transferred to rhodamine group which emit fluorescence at 585 nm with 197 fold emission enhancement and fluorescence efficiency of E = 0.98 (Fig. 4). The 'turn on' emission observed on subsequent addition of Hg^{2+} ions can also be seen by the naked eye (Fig. 4, inset). This result corroborates the idea of through bond energy transfer. Thus, the mechanism of energy transfer from HPB based donor to rhodamine acceptors in presence of Hg^{2+} ions is strongly dependent upon the nature of solvent. We believe that ring opening of the spirolactam structure is solvent assisted in protic environment, and hydrogen bonding between solvent and acceptor moiety prevents donor and acceptor fragments from becoming planar, and thus, the TBET process is facilitated (Scheme 5).

Under the same set of conditions as used for compounds **5** and **7**, we recorded the fluorescence of equimolar solution of derivative **6** (donor) and rhodamine B (acceptor) in methanol. The fluorescence spectrum exhibits the individual emission band at 426 nm, corresponding to derivative **6** only. No fluorescence corresponding to rhodamine group was observed at λ_{ex} = 290 nm (ESI, Fig. S21†) which shows that there is no intermolecular resonance energy transfer between hexaphenylbenzene (donor) and rhodamine (acceptor). Thus, the advantage of the TBET system for energy transfer is obvious.

Furthermore, the operation of through bond energy transfer mechanism in the presence of Hg^{2+} ions in derivative **5** in EtOH, *n*-PrOH and *n*-BuOH and the increase in fluorescence emission enhancement in the same order as the proton donating ability of these solvents *i.e.* *n*-butanol (42 fold) (ESI, Fig. S9†), *n*-propanol (68 fold) (ESI, Fig. S10†), ethanol (75 fold) (ESI, Fig. S11†) and methanol (197 fold), confirm above assumption regarding solvent assisted TBET process. The fluorescence enhancement factor for derivative **5** in presence of Hg^{2+} ions in MeOH (197 folds) is higher than enhancement factors (Table 1) of derivative **5** in THF and CH_3CN in presence of Hg^{2+} ions, thus, confirming the 98% energy transfer efficiency of cassette **5** in MeOH in presence of Hg^{2+} ions. Derivative **7** also exhibits through bond energy transfer in the presence of Hg^{2+} ions in methanol (130 folds) (Fig. 5), *n*-butanol (7.5 folds) (ESI, Fig. S12†), *n*-propanol (10 folds) (ESI, Fig. S13†) and ethanol (25 folds) (ESI, Fig. S14†). The solution of compound **7** in MeOH is non-fluorescent ($\phi = 3.4 \times 10^{-3}$) and addition of incremental amounts of Hg^{2+}ions (0.1–150 equiv.) to the solution of receptor **7** leads to appearance of an emission band due to rhodamine (acceptor) moiety with 130 fold emission enhancement at 585 nm (ϕ = 0.46) along with the bright yellow fluorescence visible to the naked eye (inset, Fig. 5). The fluorescence efficiency of compound **7** in methanol comes out to be E = 0.92. However, in comparison to derivative **5**, through bond energy transfer in the case of derivative **7** in protic media is 92%. It is proposed that in derivative **7**, conjugation across the donor and acceptor moieties is more facilitated due to presence of six rhodamine moieties at the periphery which restricts rotation of the phenyl rings around their own axis, thus, making derivative **7** a weaker candidate for TBET in comparison to derivative **5**. The detection limits of compound **5** and **7** as fluorescent sensors for the analysis of Hg^{2+} ions were found



Scheme 5 Hg^{2+} induced TBET off–on in protic solvents.

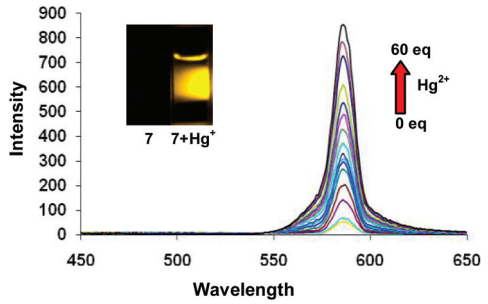


Fig. 5 Fluorescence response of receptor **7** (1 μM) on addition of Hg^{2+} (1–60 equiv.) in methanol, λ_{ex} = 290 nm and the emission intensity of receptor **7** (1 μM) at 585 nm as a function of Hg^{2+} ions. Inset shows the 'turned on' fluorescence of compound **7** on addition of Hg^{2+} ions.

to be 50×10^{-9} M and 10×10^{-8} M, respectively (ESI, Fig. S15†) which are sufficiently low for the detection of nano-molar concentrations of Hg^{2+} ions as found in many chemical systems.

Furthermore, the fluorescence spectra of model compound **11** in THF shows very weak emission band at 455 nm due to the HPB group when excited at 290 nm and addition of incremental amounts of Hg^{2+} ions (0.1–100 μM) to the solution of receptor **5** in THF leads to slight decrease in intensity of the emission band at 455 nm, suggesting no energy transfer from donor HPB unit to acceptor rhodamine moiety (ESI, Fig. S22†). Besides, no orange colour fluorescence was observed with the naked eye (ESI, Fig. S22,† inset) on addition of Hg^{2+} ions. This indicates that the band at 580 nm corresponds to double frequency peak. This result shows that derivative **11** having a rhodamine unit linked to HPB core without any spacer behaves as one planar conjugated molecule.

To test if the proposed complexation of compound **5** and **7** with Hg^{2+} ions could be reversed we also carried out a reversibility experiment. The addition of tetrabutylammonium iodide (TBAI) to the solutions of **5**–Hg^{2+} (1.0 μM in methanol) and **7**–Hg^{2+} complexes (1.0 μM in methanol) resulted in quenching of their respective fluorescence intensities. The quenching of fluorescence is due to the strong affinity of iodide ions for the Hg^{2+} ions which is responsible for decomplexation of receptor–Hg^{2+} complex *i.e.* Hg^{2+} ions are not available for binding with receptor. Further addition of Hg^{2+} ions revives the respective fluorescence emission indicating the reversible behaviour of both derivatives **5** and **7** for Hg^{2+} ions (ESI, Fig. S16 and S17†).

We also tested the fluorescence response of **5** and **7** to the other metal ions such as Fe^{3+}, Fe^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Ag^{+}, Co^{2+}, Mg^{2+}, Li^{+}, Na^{+}, and K^{+} in THF, however, no significant variation in the fluorescence spectra of **5** and **7** was observed with any other metal ion except Fe^{3+} and Fe^{2+} which also induce similar fluorescence emission but to a small extent (ESI, Fig. S7†). To check the practical ability of compound **5** and **7** as a Hg^{2+} selective fluorescent sensor, we carried out competitive experiments in the presence of Hg^{2+} at 50 equiv. and 100 equiv., respectively, mixed with Fe^{3+}, Fe^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Ag^{+}, Co^{2+}, Mg^{2+}, Li^{+}, Na^{+}, and K^{+} (100 equiv. each). No significant variation in the fluorescence emission was observed by comparison with or without the other metal ions (ESI, Fig. S8†).

To elucidate the binding mode of receptor **5** with Hg^{2+} ions, the ^{1}H NMR spectrum of its complex with mercury perchlorate was also recorded. The downfield shifts of 0.24 and 0.12 ppm corresponding to the protons of NCH_2CH_3 and NCH_2CH_3, respectively, and the aromatic protons of the rhodamine moieties of receptor **5** in the presence of 1.0/2.0 equiv. of Hg^{2+} ions (ESI, Fig. S18†) indicate the transformation of non-fluorescent spirocyclic form of rhodamine moiety in receptor **5** to the fluorescent ring opened amide form (Scheme 4). Thus from this NMR study, we may conclude that mercury is interacting with receptor **5** as supported by fluorescence studies. The 1 : 2 stoichiometry between compound **5** and Hg^{2+} ions was confirmed by the Job's plot (ESI, Fig. S19†). The binding constant (log β) was found to be 9.58 ± 0.05, inferred from the nonlinear regression analysis program SPECFIT (global analysis system V3.0 for 32-bit Windows system).

Cyclic voltammogram of **5** [CH_2Cl_2, $c = 1 \times 10^{-3}$ M, $(n\text{-Bu})_4NClO_4$ as supporting electrolyte using a glassy carbon working electrode, a (Ag/Ag^{+}) reference electrode, and a Pt wire counter electrode] exhibits three electrochemical oxidation waves at $E_{1/2}$ = −1.60 V, 0.74 V and 1.53 V (ESI, Fig. 20A†). On addition of 2 equiv. of Hg^{2+} ions, the cyclic voltammogram exhibits a shift in these oxidation waves to −1.414 V, 0.50 V and 1.42 V, respectively (ESI, Fig. 20B†). These shifts in oxidation waves toward lower potential in presence of Hg^{2+} ions indicate the decrease in oxidation potential of derivative **5** due to the formation of complex between derivative **5** and Hg^{2+} ions.

Conclusion

In conclusion, we synthesized hexaphenylbenzene derivatives **5** and **7** incorporating rhodamine moieties. Derivatives **5** and **7** exhibit fluorescence resonance energy transfer through space (FRET) in aprotic solvents and through bond energy transfer (TBET) in protic solvents only in the presence of Hg^{2+} ions among various metal ions such as Cu^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, Ag^{+}, Ba^{2+}, Mg^{2+}, K^{+}, Na^{+}, and Li^{+}. Derivative **7** exhibits more efficient FRET efficiency in the presence of Hg^{2+} ions in THF and CH_3CN than that of derivative **5** whereas derivative **5** displays nearly perfect through bond energy transfer efficiency in the presence of Hg^{2+}ions in MeOH.

Experimental

General experimental methods

All metal perchlorates were purchased from Aldrich and were used without further purification. Potassium carbonate, ethanol and tetrabutylammonium salts of anions were purchased from S.D. Fine Chemicals. THF was dried over sodium metal and benzophenone before it was used for analytical studies. Acetonitrile (HPLC grade) and methanol (HPLC grade) were used for analytical studies. All the fluorescence spectra were recorded on SHIMADZU 5301 PC spectrofluorimeter. UV spectra were

recorded on Shimadzu UV-2450PC spectrophotometer with a quartz cuvette (path length: 1 cm). The cell holder was thermostatted at 25 °C. Elemental analysis was done using Flash EA 1112 CHNS/O analyzer of Thermo Electron Corporation. ^{1}H and ^{13}C NMR spectra were recorded on JEOL-FT NMR-AL 300 MHz spectrophotometer using $CDCl_3$ and DMSO-d_6 as solvent and TMS as internal standards. Data are reported as follows: chemical shifts in parts per million (δ), multiplicity (s = singlet, br = broad signal, d = doublet, m = multiplet), coupling constants (Hz), integration, and interpretation. All spectrophotometric titration curves were fitted with SPECFIT 32 software.

Experimental details of determining detection limit

To determine the detection limit, the fluorescence titration of compound **5** with Hg^{2+} ions was carried out by adding aliquots of mercury solution of micromolar concentration and the fluorescence intensity as a function of Hg^{2+} ions added was then plotted. From this graph the concentration at which there was a sharp change in the fluorescence intensity multiplied with the concentration of receptor **5** gave the detection limit.

Experimental details

Synthesis of compounds **1**, **2** and **6**: Compounds **1** and **2** were synthesized according to the literature procedures. Compound **6** was synthesized according to the procedure previously developed in our lab.

Synthesis of compound 3. To a solution of **1** (0.3 g, 0.43 mmol) and **2** (0.23 g, 1.08 mmol) in THF were added K_2CO_3 (0.48 mg, 3.5 mmol), distilled H_2O (3 mL), and [Pd(Cl)$_2$(PPh$_3$)$_2$] (0.12 g, 0.17 mmol) under argon and the reaction mixture was refluxed overnight. The THF was then removed under vacuum and the residue so obtained was treated with water, extracted with dichloromethane, and dried over anhydrous Na_2SO_4. The organic layer was evaporated and the compound was purified by column chromatography using ethyl acetate as an eluent to give compound **3** which was further recrystallized from methanol to provide 0.58 g of white solid (yield 53%). mp: 220 °C. ^{1}H NMR: δ 6.64 (d, 4H, J = 8 Hz, ArH), 6.81–6.85 (m, 24H, ArH), 7.05 (d, 4H, J = 8 Hz), 7.24 (d, 4H, J = 7.5 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): 80.51, 118.52, 124.77, 125.14, 125.20, 126.54, 126.64, 127.15, 127.20, 131.42, 131.84, 135.47, 136.87, 137.25, 139.35, 139.58, 140.42, 140.57, 140.62, 152.61. FAB-MS: 717 $(M + 1)^+$; Anal. Calcd for $C_{54}H_{40}N_2$: C, 90.47; H, 5.62; N, 3.91. Found: C, 90.32; H, 5.69; N, 3.99.

Synthesis of compound 5. The acid chloride **4** (0.1 g, 0.21 mmol) was dissolved in dry dichloromethane (10 mL). To the above solution was added the solution of compound **3** (0.07 g, 0.09 mmol) in dichloromethane and triethylamine. The reaction mixture was stirred overnight at room temperature. The mixture so obtained was treated with water, extracted with dichloromethane, and dried over anhydrous Na_2SO_4. The organic layer was evaporated under reduced pressure and the crude product was purified by column chromatography (EtOAc : hexane, 7 : 3) and recrystallised from methanol to give 0.081 g of white solid **5** (yield 63%): mp >260 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.13 (t, 24H, J = 6.6 Hz, NCH_2CH_3), 3.29 (q, 16H, J = 6.0 Hz, NCH_2CH_3), 6.19–6.27 (m, 6H, ArH), 6.60 (d, 4H, J = 8.4 Hz, ArH), 6.79–6.81 (m, 36H, ArH), 6.99 (d, 2H, J = 7.8 Hz, ArH), 7.16 (d, 2H, J = 7.8 Hz, ArH), 7.46 (br, 4H, ArH), 7.97 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 13.03, 44.72, 98.34, 106.89, 108.53, 123.69, 124.34, 125.44, 125.53, 126.00, 126.93, 127.01, 127.18, 128.42, 129.14, 131.25, 132.13, 133.15, 136.07, 137.39, 138.89, 140.23, 140.80, 140.90, 140.98, 141.07, 149.18, 153.44, 153.93, 169.12; MALDI-MS: 1565 (M^+). Anal. Calcd for $C_{110}H_{96}N_6O_4$: C, 84.37; H, 6.18; N, 5.37. Found: C, 84.54; H, 6.22; N, 5.45.

Synthesis of compound 7. To the stirred solution of acid chloride **4** (0.1 g, 0.22 mmol) in DMF (HPLC) (10 mL) was above solution was added the solution of hexamine **6** (0.07 g, 0.09 mmol) in DMF and triethylamine. The reaction mixture was stirred overnight at room temperature. The mixture so obtained was treated with water, extracted with dichloromethane, and dried over anhydrous Na_2SO_4. The organic layer was evaporated under reduced pressure and the crude product was purified by column chromatography (EtOAc) followed by the recrystallization from methanol to give 135 mg of **7** (yield 50%): mp >260 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.13–1.11 (m, 72H, NCH_2CH_3), 3.30–3.28 (m, 48H, NCH_2CH_3), 6.21–6.24 (m, 18H, ArH), 6.62–6.57 (m, 18H, ArH), 6.74 (br, 24H, ArH), 6.98 (br, 12H, ArH), 7.25–7.14 (m, 18H, ArH), 7.47 (d, 12H, ArH), 7.98 (br, 6H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$: DMSO-d_6) 12.24, 43.70, 97.19, 105.55, 107.82, 110.38, 122.8, 124.00, 125.87, 126.28, 128.22, 129.91, 131.44, 135.46, 139.92, 148.16, 152.24, 166.85, 170.02. MALDI-MS: 3630.8 ($M + 2^+$). Anal. Calcd for $C_{246}H_{228}N_{18}O_{12}$: C, 81.43; H, 6.33; N, 6.95. Found: C, 81.13; H, 6.40; N, 7.16.

Synthesis of compound 10. Tetraphenylcyclopentadienone **8** (0.9 g, 2.35 mmol) and phenyl acetylene 9 (0.5 g, 2.59 mmol) were suspended in minimal amount of diphenylether and refluxed overnight under nitrogen atmosphere. The reaction mixture so obtained was cooled to room temperature, poured into methanol and the solid hence obtained was filtered. The crude product was purified by column chromatography (chloroform–hexane, 1 : 4) to afford 0.56 g of light yellow solid **10** (yield = 60%) which was further recrystallized in methanol. Mp >260 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.32 (s, 2H, NH_2), 6.19 (d, 2H, J = 9 Hz, ArH), 6.57 (d, 2H, J = 9 Hz, ArH), 6.79–6.86 (m, 25H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 85.90, 87.82, 90.48, 96.82, 114.17, 118.29, 125.40, 125.49, 126.92, 126.97, 131.84, 131.89, 132.68, 136.25, 140.65, 141.99, 143.73, 154.05, 156.70. MALDI-MS: 549.2769 (M^+). Anal. Calcd for $C_{42}H_{31}N$: C, 91.77; H, 5.68; N, 2.55 Found: C, 91.43; H, 5.71; N, 2.48.

Synthesis of compound 11. The acid chloride (0.07 g, 0.14 mmol) was dissolved in dry dichloromethane (10 mL). To the above solution was added the solution of compound **10** (0.07 g, 0.14 mmol) in dichloromethane and triethylamine. The reaction mixture was stirred overnight at room temperature. The mixture so obtained was treated with water, extracted with dichloromethane, and dried over anhydrous Na_2SO_4. The organic layer was evaporated under reduced pressure and the crude product was purified by column chromatography

(hexane : EtOAc, 95 : 5) and recrystallised from methanol to give 60 mg of off-white solid **11** (yield 44%): mp >260 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (br, 1H, ArH), 7.40–7.43 (m, 2H, ArH), 7.03–7.06 (m, 1H, ArH), 6.82–6.64 (m, 25H, ArH), 6.47–6.52 (m, 4H, ArH), 6.21–6.25 (m, 6H, ArH), 3.33 (q, 8H, J = 8 Hz, NCH_2CH_3), 1.17 (t, 12H, J = 7.5 Hz, NCH_2CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.62, 44.27, 67.25, 76.36, 76.59, 77.00, 77.20, 77.42, 97.86, 106.35, 108.00, 123.10, 123.87, 125.06, 125.14, 125.64, 126.49, 126.59, 127.94, 128.84, 130.84, 131.30, 131.43, 132.57, 133.63, 138.99, 140.09, 140.12, 140.24, 140.64, 148.56, 152.97. MS: 974 (M^+). Anal. Calcd for $C_{70}H_{59}N_3O_2$: C, 86.30; H, 6.10; N, 4.31. Found: C, 85.98; H, 6.15; N, 4.22.

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Notes and references

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