

Figure 3 Energy diagram of the MO levels of BAPTA-NI (Ligand) and its complex with calcium cation (Complex). The blue arrow indicates the long-wavelength electron transition.

groups is 2.27–2.30 Å, while the distances to the nitrogen atoms of the amino groups are 2.89 Å and 2.95 Å [for N–C(1) and N–C(7), respectively], as well as 2.71 Å [O–C(8)] and 2.63 Å [O–C(9)] to the oxygen atoms of the ethylene glycol bridge. Based on the calculation results, an energy diagram was built (Figure 3). It demonstrates the processes that occur during the photoexcitation of a free sensor molecule and its complex. Figure 4 shows the electron density distribution over the boundary orbitals in the molecules of the BAPTA-NI sensor and the calcium complex.

As one can see from the molecular orbital diagram, the long-wavelength electronic transition in the sensor molecule occurs from the HOMO to the LUMO located on the naphthalimide moiety. In this case, photoinduced electron transfer to a single-occupied HOMO of the molecule from the HOMO(-1) orbital located on the receptor site is possible in the system. Thus, the PET process is a probable relaxation channel of the excited state. Binding of the ligand with the calcium cation results in a significant decrease in the energy of the orbitals localized on the receptor arene rings. However, the orbital belonging to the naphthalimide chromophore still remains the HOMO(-1) and the electron transfer process is still possible in the molecule.

In conclusion, BAPTA-NI, a new derivative of 4-methoxy-1,8-naphthalimide equipped with bis(*o*-aminophenoxy)ethane-*N,N,N',N'*-tetraacetate receptor moiety for the binding of calcium

cations, was obtained. The observed fluorescence buildup upon Ca^{2+} binding is due to the suppression of the PET process in the free ligand. Using the optical and NMR spectroscopy methods, the formation of one type of complex with a composition of 1 : 1 was established, so BAPTA-NI may be qualified as a fluorescent PET chemosensor for the Ca^{2+} cation.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.05.024.

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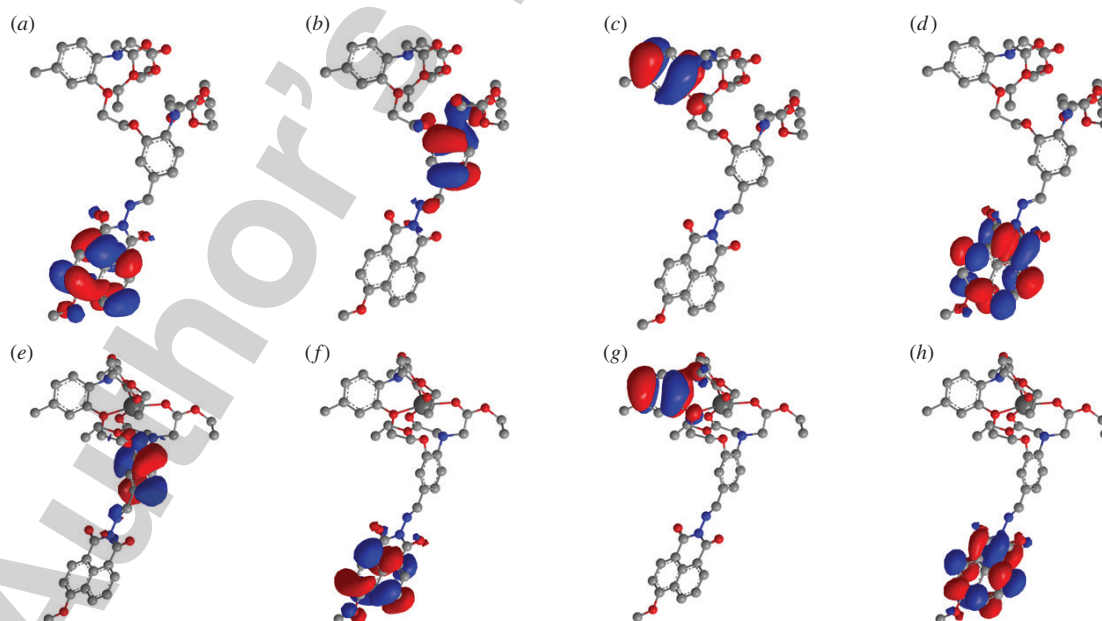


Figure 4 Electron density distribution over the boundary orbitals of (a)–(d) BAPTA-NI (Ligand) and (e)–(h) its complex with calcium cation (L)- Ca^{2+} ; (a), (e) HOMO(-2); (b), (f) HOMO(-1); (c), (g) HOMO; (d), (h) LUMO.