

Silicon photosensitisation using singlet/triplet emitters

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The possibility for the production of electron-hole (e-h) pairs in a semiconductor via resonance energy transfer from molecules on the surface was originally proposed by Dexter.¹ The proposed sensitisation can result in significant savings of the expensive semiconductor material used in solar cells and could potentially introduce new solar cell paradigms. The proposed scheme separates the photovoltaic process into two separate steps; An absorption and a charge generation step which can be treated like two independent processes.²

Since Dexter's proposal numerous experimental studies have demonstrated quenching of molecular fluorescence near the surface of silicon from evaporated dye layers,³⁻⁵ quantum dots,⁶ Langmuir-Blodgett (LB) monolayers,⁷⁻⁹ and dye loaded zeolite structures.¹⁰ Most of the cases of observed fluorescence quenching could be attributed to photon tunnelling,¹¹ a form of energy transfer via coupling of the evanescent field for distances up to 30 nm and not a Förster type energy transfer which occurs via a near field interaction in the subnanometer scale. A recent study demonstrated a Förster type energy transfer with protoporphyrin molecules directly attached on the surface of silicon for distances to the surface of silicon of less than 2nm.¹² All these studies have been performed using singlet type of emitters and have demonstrated their potential application in new solar cell designs.^{13,14}

In his original proposal Dexter suggested the benefits of using triplet type of emitters such as: long exciton diffusion lengths, which will allow the exciton's diffusion to the surface of the semiconductor; the possibility of singlet fission, which could potentially produce 2 x e-h pairs from a single excitation. In recent years a lot of research has been focussed in studying triplet excitations for applications in solar cells such as singlet fission¹⁵ or up conversion via triplet-triplet annihilation¹⁶ but observing triplet emission quenching on the surface of silicon has not been demonstrated before.

In this paper, we will show phosphorescence quenching observed from Langmuir-Blodgett monolayers of organometallic complexes (Fig. 1) deposited on the surface of silicon as a function of distance (Fig. 2). We have used steady state (Fig. 3) and time resolved emission measurements (Fig. 6) of the excited state lifetime and have observed a significant quenching over 90% from the free unquenched phosphorescence lifetime. Fluorescence Lifetime Imaging (FLIM) reveals the structure of the deposited organometallic complex monolayers on the surface of silicon, which is the result of hydrophobic forces acting on the monolayer (Fig. 5).

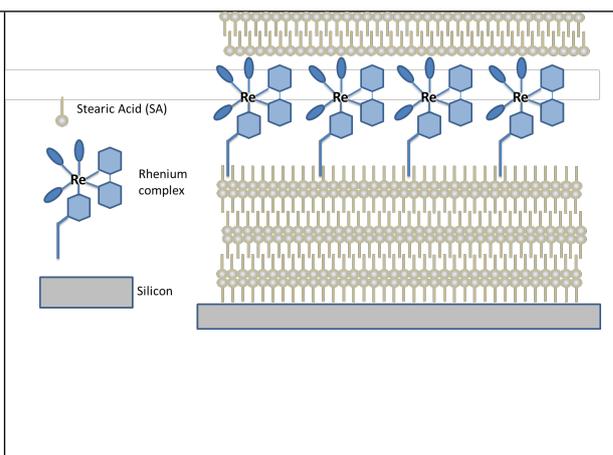
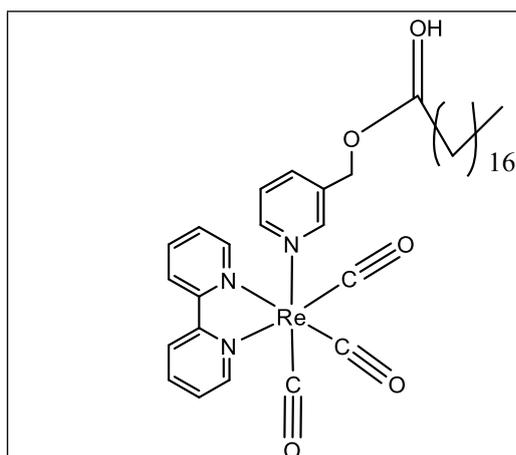


Fig. 1 Chemical structure of the Rhenium complex used in this study for the preparation of the Langmuir Blodgett monolayers on silicon substrates. **Fig. 2** Structure of the Rhenium monolayer for the distance dependence study on silicon using Stearic Acid (SA) spacers.

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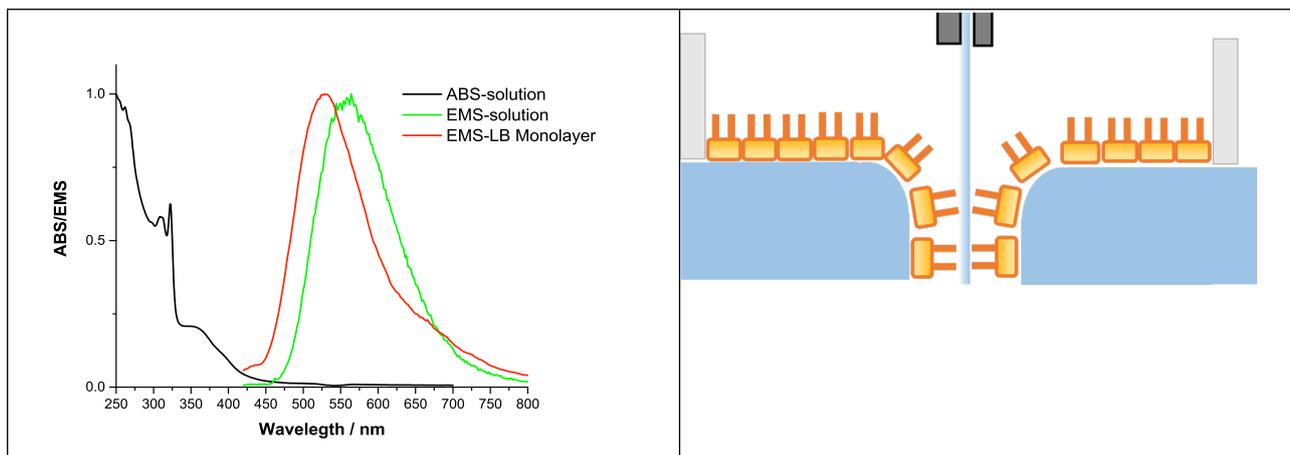


Fig. 3 Absorption and emission spectra of the Rhenium complex in solution and deposited on glass as a monolayer film.

Fig. 4 Langmuir Blodgett technique; The film is held at constant pressure and as the glass slide or silicon substrate moves through the water surface, a monolayer is deposited on the surface of the glass.

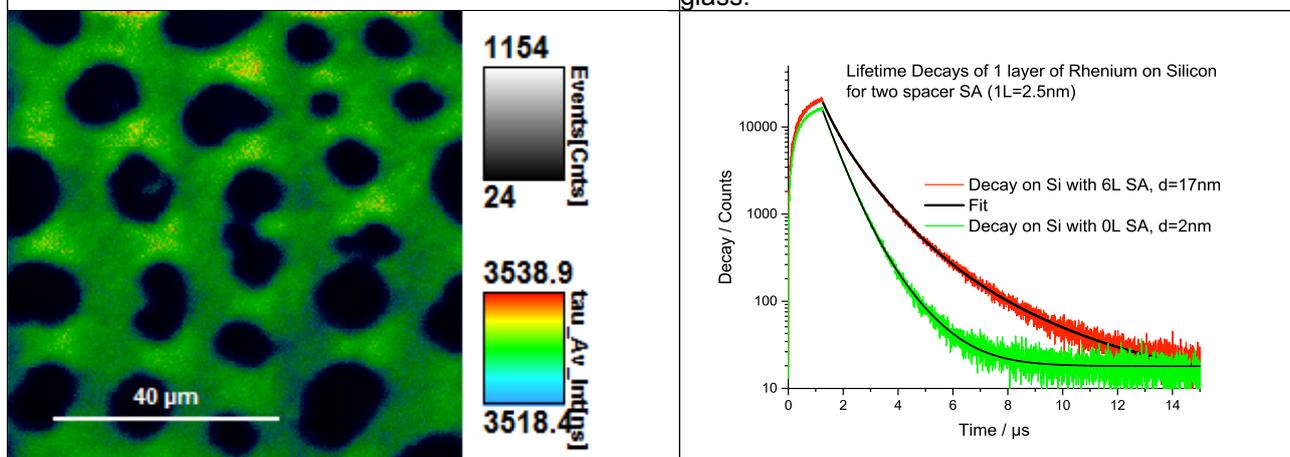


Fig. 5 FLIM image of a monolayer of Rhenium on the surface of silicon.

Fig. 6 Decay lifetimes for two separate stearic acid spacer distances for a Rhenium monolayer deposited on a silicon substrate.

References

- 1 D. L. Dexter, *J. Lumin.*, 1979, **18–19**, 779–784.
- 2 T. Markvart, *Prog. Quantum Electron.*, 2000, **24**, 107–186.
- 3 T. Hayashi, T. G. Castner and R. W. Boyd, *Chem. Phys. Lett.*, 1983, **94**, 461–466.
- 4 P. M. Whitmore, A. P. Alivisatos and C. B. Harris, *Phys. Rev. Lett.*, 1983, **50**, 1092.
- 5 A. A. P., M. F. Arndt, D. H. Waldeck and C. B. Harris, *J. Chem. Phys.*
- 6 M. T. Nimmo, L. M. Caillard, W. De Benedetti, H. M. Nguyen, O. Seitz, Y. N. Gartstein, Y. J. Chabal and A. V. Malko, *ACS Nano*, 2013, **7**, 3236–3245.
- 7 M. I. Sluch, A. G. Vitukhnovsky and M. C. Petty, *Phys. Lett. A*, 1995, **4**, 61.
- 8 L. Danos, R. Greef and T. Markvart, *Thin Solid Films*, 2008, **516**, 7251–7255.
- 9 L. Danos and T. Markvart, *Chem. Phys. Lett.*, 2010, **490**, 194–199.
- 10 S. Huber and G. Calzaferri, *Chemphyschem*, 2004, **5**, 239–42.
- 11 L. Fang, K. S. Kiang, N. P. Alderman, L. Danos and T. Markvart, *Opt. Express*, 2015, **23**, A1528–A1532.
- 12 N. Alderman, L. Danos, L. Fang, M. Grossel and T. Markvart, *Chem. Commun.*, 2017, **53**, 12120–12123.
- 13 W. Peng, S. M. Rupich, N. Shafiq, Y. N. Gartstein, A. V. Malko and Y. J. Chabal, *Chem. Rev.*, 2015, **115**, 12764.
- 14 V. M. Agranovich, Y. N. Gartstein and M. Litinskaya, *Chem. Rev.*, 2011, **111**, 5179–5214.
- 15 M. B. Smith and J. Michl, *Chem. Rev.*, 2010, **110**, 6891–936.
- 16 T. F. Schulze and T. W. Schmidt, *Energy Environ. Sci.*, 2015, **8**, 103–125.