# Magnetic Field Effects on Triplet-Triplet Annihilation in Solutions: Modulation of Visible/NIR Luminescence

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## Abstract

Photon upconversion based on sensitized triplet-triplet annihilation (TTA) presents interest for such areas as photovoltaics and imaging. Usually energy upconversion is observed as *p*-type delayed fluorescence from molecules whose triplet states are populated *via* energy transfer from a suitable triplet donor, followed by TTA. Magnetic field effects (MFE) on delayed fluorescence in molecular crystals are well known; however, there exist only a few examples of MFE on TTA in solutions, and all of them are limited to UV-emitting materials. Here we present MFE on TTA-mediated visible and near infrared (NIR) emission, sensitized by far-red absorbing metalloporphyrins in solutions at room temperature. In addition to visible delayed fluorescence from annihilator, we also observed NIR emission from the sensitizer, occurring as a result of triplet-triplet energy transfer back from annihilator, termed "delayed phosphorescence". This emission also exhibits MFE, but opposite in sign to the annihilator fluorescence.

## Keywords

Magnetic Field Effects; *p*-type Delayed Fluorescence; Delayed Phosphorescence; Spin Dynamics; Triplet-Triplet Annihilation; Porphyrin; Tetrabenzoporphyrin

Magnetic field effects (MFE)[1] present an attractive opportunity to impose control over excited electronic states of molecules, drawing attention from many areas of technology. For example, in optical imaging magnetic control over probes' emissivity may serve to enhance spatial resolution,[2–3] while in the medical field the ability to magnetically modulate sensitized generation of singlet oxygen could be a valuable asset for photodynamic therapy.[4] The key to such applications are molecules with strong optical transitions in the visible/near infrared (NIR) spectral region and excited states responsive to magnetic fields.

Three kinds of MFE on molecular luminescence are presently known. The first involves emission from exciplex states existing in equilibrium with radical pairs (RP) formed upon photoinduced electron transfer (PET).[5–6] External magnetic field modulates spin dynamics within an RP, affecting the charge recombination channel coupled to the formation of emissive exciplexes. In some cases fluorescence from the parent local singlet state may also be modulated.[6] Another kind, reported recently, is the MFE on phosphorescence, whereby an RP is included into a pathway leading to the formation (or decay) of a triplet state localized on a strongly phosphorescent chromophore.[7] The third kind is the MFE on triplet-

triplet annihilation (TTA) and subsequent *p*-type delayed fluorescence.[8–9] This effect has been observed in molecular crystals and studied extensively by Merrifield and co-workers,[8–11] and soon thereafter reported for photosensitized TTA in solutions.[12–13] Several related studies, including MFE's on quenching of delayed fluorescence by oxygen[14–15] and electro-generated luminescence[16–17] have also been published.

During the past decade significant progress has been made in the TTA field,[18–20] and many efficient photosensitized upconversion systems have been developed, including ones with absorption in the red and NIR spectral regions.[21–25] In one such system, MFE on TTA in polymeric membranes has been observed,[26] and more recently a study of MFE on fluorescence dynamics in closely related singlet fission systems has been published.[27] Here we report MFE's in solution-based TTA systems where the role of photosensitizers is played by strongly red-absorbing -extended metalloporphyrins. Such systems may present interest for bio-imaging applications,[28] where multiphoton excitation by low-power NIR sources is especially attractive because of low risk of photodamage and reduced scattering. In addition to the well-known MFE on delayed fluorescence we also report a new effect, which is manifested by magnetic modulation of the emission originated from the sensitizer itself, termed "delayed phosphorescence." The two MFE's were found to exhibit opposite signs.

The process leading to photo-sensitization of delayed fluorescence involves in its initial step triplet-triplet energy transfer (TTET) from donor-sensitizer to acceptor-annihilator (Fig. 1). Sensitizers are usually chosen to be molecules efficiently forming long-lived triplet states *via* fast intersystem crossing (ISC). In this regard, Pt and Pd porphyrins are especially attractive, as they are characterized by very strong spin-orbit coupling and form triplet states with nearly unity efficiency.[29–30] The corresponding upconversion gaps, reported for porphyrin-based TTA systems, reach up to ~0.8 eV.[18]

In a well-designed TTA system the triplet state of the sensitizer ($^{S}T_1$) should be efficiently quenched by the annihilator *via* TTET. Therefore, little or no phosphorescence from the donor (provided the donor triplet state is phosphorescent) should be observed. However, if the triplet state of the acceptor $^{A}T_1$ is energetically close to $^{S}T_1$, and its own decay is slower than that of the donor phosphorescence, $k_T \ll k_{phos}$, the equilibrium between the two states may be established, leading to the appearance of "delayed phosphorescence." This kind of emission is usually not mentioned in the TTA literature, however in our systems it has been detected and found to be magnetically sensitive.

The theory of MFE on TTA was originally developed by Merrifield[9–10] and Suna[31] for triplet excitons in molecular crystals, and later extended by Atkins and Evans[32] to include the dependence of TTA on rotational and translational parameters of freely moving triplet molecules in solution. Recently, an extension of the theory has been applied to systems undergoing singlet exciton fission.[27] The rate of TTA *via* the singlet channel – the one that leads to the appearance of delayed fluorescence, – depends on the distribution of singlet character over the nine spin states of the interacting triplet-triplet (TT) pair: singlet, triplets and quintets. Based on kinetic arguments, more uniform distribution leads to a higher recombination rate and *vice versa* (singlet dilution principle).[10] For a pair of equivalent triplets, i.e. the case most relevant to photon upconversion *via* TTA, symmetry considerations dictate that only six out of nine spin states of the TT pair (singlet and quintets) can possess singlet character regardless of the field strength.[9] The triplet states of the pair are able to enter only the triplet recombination channel, which is field-independent. The singlet character distribution changes from zero-field, when the spin is quantized along the axes of the ZFS (zero-field splitting) tensor in each triplet molecule, to the high field limit, when the states of the pair are derived from the pure spin states of the triplet components, split by the Zeeman interaction. In low field, the singlet character is distributed

more uniformly over the pair sates, leading to a higher rate of recombination and hence higher yield of delayed fluorescence. In the high field limit, the singlet becomes "concentrated" on just two pair states, and the yield of fluorescence decreases. Importantly, fewer annihilator triplets ($^A T_1$) entering the singlet recombination channel mean higher population of the sensitizer triplets ($^S T_1$) *via* the triplet-triplet energy transfer equilibrium (Fig. 1). Thus, one should expect an increase in the yield of delayed phosphorescence with application of the field.

In this work we used Pd and Pt tetrabenzoporphyrins (MTBP) as triplet donors (sensitizers) and perylene as a triplet acceptor (annihilator) (Fig. 2A). TTA systems based on MTBP's and other -extended porphyrins have been studied in the past.[21–24] It has been confirmed that in all such systems fluorescence signal has second order, i.e. it occurs upon absorption of two photons (*p*-type delayed fluorescence).[22] Using the oxidative aromatization method,[33–35] MTBP's can be conveniently synthesized having various substituents in the macrocycle, thus ensuring compatibility with a large selection of solvents. In the present work experiments were performed in N,N'-dimethylformamide (DMF).

The absorption and emission spectra of the components are shown in Fig. 2B. The energy levels of the first excited triplet states of Pd and PtTBP's ($^S T_1$) are 1.55[36] and 1.61 eV,[37] respectively, while that of perylene ($^A T_1$) is 1.53 eV.[38] The charge separated states, which could form potentially as a result of photoinduced electron transfer (PET), are significantly higher in energy than the triplet states. Therefore, PET could not be a significant pathway in these systems. Pd and PtTBP are known to be brightly phosphorescent at ambient temperatures, and their triplet states are efficiently quenched by molecular oxygen, underpinning their application in oxygen sensing and imaging.[36, 39–40] Accordingly, all experiments were conducted in rigorously deoxygenated solutions.

In the absence of perylene and oxygen, phosphorescence of Pd and PtTBP (~5 μM) decays mono-exponentially with lifetimes of ~200 μs and 30 μs and quantum yields of 0.03 and 0.12, respectively (measured against fluorescence of Rhodamine 6G in EtOH, $\varphi_{fl}$=0.94).[41] In mixtures with perylene, excitation of MTBP's at the Q-bands ($S_0$–$S_1$) results in phosphorescence from MTBP's along with delayed fluorescence from perylene (Fig. S1A). The decays of the phosphorescence were pronouncedly biphasic (Fig. S1B), and the decay time of the faster ("prompt") component matched the rise time of the perylene delayed fluorescence. As expected, increase in the perylene concentration caused decrease in the lifetime of the "prompt" phosphorescence in agreement with enhanced bimolecular quenching (Fig. S1C).

The slower component of the phosphorescence decay is a manifestation of the delayed phosphorescence, occurring as a result of TTET-mediated equilibrium between the sensitizer and acceptor triplet states, $^S T_1$ and $^A T_1$ (Fig. 1). Indeed, the time constants of the slower decays for both PtTBP and PdTBP (290 μs and 540 μs, respectively; perylene concentration 100 μM) were longer than the corresponding decays in the absence of perylene. The TTET equilibrium is facilitated by the proximity of the triplet energy levels of MTBP's and perylene as well as by the long lifetime of the perylene triplet state ( ~5000 μs).[24, 42] Intramolecular delayed phosphorescence *via* TTET in porphyrin-based covalent systems has been observed previously,[43–44] however, in the present case the reaction is bi-molecular in nature. Accordingly, the decay rate of the delayed phosphorescence, as well as of the delayed fluorescence, increased with an increase in the concentration of perylene, which led to a higher rate of depletion (self-quenching *via* annihilation) of the perylene triplet population (Fig. S1C).

Magnetically Affected Reaction Yield (MARY) spectroscopy was further employed to study MFE on the TTA in MTBP/perylene systems. Our custom-built setup consists of a fiber-optic time-domain phosphorometer and a tunable magnet (see ref [7] for details). MARY spectra (integrated luminescence intensity *vs* field strength; in the case of delayed phosphorescence, the slow portion of the biphasic decay was integrated) were recorded upon excitation of metalloporphyrins (sensitizers) at their Q-band maxima ($\lambda_{ex}$~635 nm). Appropriate band-pass filters were used to selectively detect delayed fluorescence (<550 nm) and phosphorescence (>730 nm).

In both cases, PdTBP/perylene and PtTBP/perylene, switching of the magnetic field "ON" caused a pronounced decrease in the delayed fluorescence (Fig. 3A, B=1T), accompanied by an increase in the delayed phosphorescence. Both signals were fully recoverable to the baseline level upon switching the field "OFF" (Fig. 3B). This reversibility confirms that the observed changes are truly effected by the magnetic field and not artifacts of the measurement. The dependencies of the fluorescence and phosphorescence on the field are opposite to each other: the fluorescence decreases with an increase in the field and the phosphorescence increases (Fig. 3C). The MFE's in Fig. 3C are quantified as the percent change in the emission intensity with application of the field: MFE(%)=100×[Y(B)−Y(0)]/Y(0), where Y(B) and Y(0) are the integrated emission intensities in the presence and absence of the magnetic field, respectively. The positive MFE on the phosphorescence *via* TTA contrasts the negative MFE in the systems where the phosphorescence is modulated *via* radical pair pathway.[7]

Due to the instrument limitations we could not examine the early time course of the delayed fluorescence signal with adequate accuracy. However, we conjecture that this curve may exhibit its own dependence on the magnetic field. Such an MFE may occur if spin polarization is present in the donor triplet state, it gets transferred from the donor to acceptor *via* TTET, and intermolecular TTA takes place prior to spin relaxation within the acceptor triplet population.[45–47] To this end, it is known that triplet states of Pt (and Pd) porphyrins, formed by $S_1 \rightarrow T_1$ ISC, are strongly spin-polarized.[48–49] At sufficiently high concentrations of perylene (~1 mM), the rise time of the fluorescence is much shorter than $10^{-6}$ s, indicating that the collisional TTET followed by the TTA likely occurs faster than spin relaxation, which has time scale of $10^{-7}$–$10^{-6}$ s.[50–51] Therefore, the slope of the rise is expected to exhibit magnetic field dependence.

Following Murai et al.,[52] we can employ the analytical model of Atkins and Evans[32] to quantitatively account for our observations. Assuming that the only magnetically sensitive parameter in TTA systems is rate constant $k_{TTA}$ (Fig. 1), the following expression holds true:[32]

$$\frac{k_{TTA}(B)}{k_{TTA}(0)} = \frac{P_{TTA}(B)}{P_{TTA}(0)} = \frac{1 + \varphi_{TTA} f_{TTA}(B)}{1 + \varphi_{TTA} f_{TTA}(0)}, \quad (1)$$

where:

$$\varphi_{TTA} = \frac{\lambda_T}{1 - \lambda_T}, \quad (2)$$

$P_{TTA}(B)$ is the probability of the TTA, $f_{TTA}(B)$ is the field-dependent parameter related to the singlet character distribution in the TT pair, and $\lambda_T$ is the reaction probability for the singlet recombination channel that accounts for delayed fluorescence. Parameters $P_{TTA}(B)$ and $f_{TTA}(B)$ (see Supporting Information and in refs. [32, 52] for details) are specific to the molecules forming the TT pairs (i.e. perylene), i.e. ZFS constants (D and E) of the triplet

state and the rotational correlation time ($\tau_r$). These values could be found in the literature.[53–55]

The integrated intensity of the delayed fluorescence ($Y_F$), which is a direct observable in our experiments, is proportional to the product of the square of the concentration of the annihilator triplet state ($[^AT_1]^2$) and the second order rate constant ($k_{TTA}$). On the other hand, the intensity of the delayed phosphorescence ($Y_P$) is proportional the product of the annihilator triplet concentration ($[^AT_1]$), the sensitizer ground state ($[^SS_0]$) and the field-independent constant ($k^{-1}_{TTET}$). Thus, we can write:

$$\frac{Y_F(B)}{Y_F(0)} = \frac{k_{TTA}(B)[^AT_1]_B^2}{k_{TTA}(0)[^AT_1]_0^2} \qquad \frac{Y_P(B)}{Y_P(0)} = \frac{[^AT_1]_B[^SS_0]_B}{[^AT_1]_0[^SS_0]_0} \approx \frac{[^AT_1]_B}{[^AT_1]_0} \quad (3)$$

where $[^AT_1]_B$, $[^SS_0]_B$, $[^AT_1]_0$ and $[^SS_0]_0$ indicate concentrations of the corresponding species under steady-state conditions (i.e. constant rate of excitation) in the presence and absence of the field, respectively. In deriving expressions (3) we assumed that the relative change in the concentration of $^SS_0$ with application of the field is negligible, which should be the case at low light intensities. Combining expressions (3) and substituting into (1) we obtain the relationship between the theoretical MFE on the TTA rate constants[32] and the experimental observables:

$$\frac{Y_F(B)}{Y_F(0)} \times \left(\frac{Y_P(0)}{Y_P(B)}\right)^2 = \frac{1 + \varphi_{TTA} f_{TTA}(B)}{1 + \varphi_{TTA} f_{TTA}(0)} \quad (4)$$

Fitting the MARY data with Eq. 4 (Fig. 4) leads to a value of $\varphi_T \sim 0.7$, which is higher than used in previous calculations,[52] but still lies within the acceptable range ($<1$).

The MFE values at B=1T (the highest accessible field in our setup) are summarized in Table 1 for the studied chromophore combinations.

The MFE on the delayed fluorescence is negative relative to the field increase and has the absolute value of ~10%, regardless of the sensitizer-porphyrin. For the systems studied, the rise and decay phases of the signal are determined by constants $k_{TTET}$ and $k_T$, while TTET is the rate-limiting step in the overall upconversion process, i.e. $k_{TTA} \gg k_{TTET}$. The magnetic modulation of the fluorescence intensity is due to the modulation of $k_{TTA}$, which is partially compensated by the changes in concentration of $^AT_1$. The MFE on the delayed phosphorescence is positive and has smaller magnitude (1–2%). This effect is solely due to the modulation of the $^AT_1$ pool, as it is affected by the modulation of the TTA channel. The decay time of the delayed phosphorescence signal is effectively increased at higher magnetic fields and, as expected, it is about two times longer than the decay time of the delayed fluorescence.

It is interesting to note that according to the recently performed studies,[27] for ensembles of TT pairs with statistical mutual orientation of chromophores, such as in solution-based systems, increase in the field up to 100–200 Gauss is predicted to distribute singlet character almost uniformly over all nine pair spin eigenstates (compared to the three states in zero-field), and hence the average rate of TTA should increase. Our MARY curves, however, do not exhibit such a low-field feature (increase in the delayed fluorescence), suggesting that parallel orientations, for which the original theoretical treatment was elaborated, are somehow preferentially formed and/or longer-lived.

In conclusion, we have demonstrated magnetic modulation of delayed fluorescence and delayed phosphorescence in solution-based TTA systems comprising perylene as annihilator

and red-absorbing -extended porphyrins as triplet sensitizers. The MFE on the delayed phosphorescence is due to the equilibrium of the porphyrin and perylene triplet state pools mediated by triplet-triplet energy transfer. The latter phenomenon bears some similarity with magnetic modulation of "prompt" fluorescence in systems where triplet excitons are produced upon singlet fission, and the equilibrium between the singlet and triplet populations is established already at early stages of the singlet decay.[27] The described results may present interest for development of new imaging and sensing approaches that combine optical and magnetic modalities. Further studies employing other combinations of sensitizer/annihilator pairs and methods for studying MFE in time-resolved fashion are underway.

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

## Acknowledgments

## References

1. Steiner UE, Ulrich T. Magnetic-Field Effects in Chemical-Kinetics and Related. Phenomena Chem Rev. 1989; 89:51–147.

2. Yang N, Cohen AE. Optical Imaging through Scattering Media via Magnetically Modulated Fluorescence. Opt Express. 2010; 18:25461–25467. [PubMed: 21164893]

3. Le Sage D, Arai K, Glenn DR, DeVience SJ, Pham LM, Rahn-Lee L, Lukin MD, Yacoby A, Komeili A, Walsworth RL. Optical Magnetic Imaging of Living Cells. Nature. 2013; 496:486–489. [PubMed: 23619694]

4. Mermut O, Diamond KR, Cormier JF, Gallant P, Ho N, Leclair S, Marois JS, Noiseux I, Morin JF, Patterson MS, Vernon ML. The Use of Magnetic Field Effects on Photosensitizer Luminescence as a Novel Probe for Optical Monitoring of Oxygen in Photodynamic Therapy. Phys Med Biol. 2009; 54:1–16. [PubMed: 19060362]

5. Schulten K, Staerk H, Weller A, Werner HJ, Nickel B. Magnetic Field Dependence of Geminate Recombination of Radical Ion Pairs in Polar Solvents. Z Phys Chem. 1976; 101:371–390.

6. Kattnig DR, Rosspeintner A, Grampp G. Magnetic Field Effects on Exciplex-Forming Systems: the Effect on the Locally Excited Fluorophore and its Dependence on Free energy. Phys Chem Chem Phys. 2011; 13:3446–3460. and references therein. [PubMed: 21180733]

7. Mani T, Tanabe M, Yamauchi S, Tkachenko NV, Vinogradov SA. Modulation of Visible Room Temperature Phosphorescence by Weak Magnetic Fields. J Phys Chem Lett. 2012; 3:3115–3119.

8. Johnson RC, Merrifield RE, Avakian P, Flippen RB. Effects of Magnetic Fields on Mutual Annihilation of Triplet Excitions in Molecular Crystals. Phys Rev Lett. 1967; 19:285–287.

9. Johnson RC, Merrifield RE. Effects of Magnetic Fields on Mutual Annihilation of Triplet Excitons in Anthracene Crystals. Phys Rev B. 1970; 1:896–902.

10. Merrifield RE. Theory of Magnetic Field Effects on Mutual Annihilation of Triplet excitons. J Chem Phys. 1968; 48:4318–4319.

11. Groff RP, Merrifield RE, Avakian P. Singlet and Triplet Channels for Triplet-Exciton Fusion in Anthracene Crystals. Chem Phys Lett. 1970; 5:168–170.

12. Faulkner LR, Bard AJ. Magnetic Field Effects on Anthracene Triplet-Triplet Annihilation in Fluid Solutions. J Am Chem Soc. 1969; 91:6495–6497.

13. Wyrsch D, Labhart H. Magnetic Field Effects on p-Type Delayed Fluorescence of 1,2-Benzanthracene in Aolution. Chem Phys Lett. 1971; 8:217–219.

14. Geacintov NE, Swenberg CE. Possible Effects of Magnetic-Fields on Quenching of Triplet Excited-States of Polynuclear Hydrocarbons by Oxygen. J Chem Phys. 1972; 57:378–389.

15. Tachikawa H, Bard AJ. Magnetic-Field Effects on Oxygen Quenching of Delayed Fluorescence of Anthracene and Pyrene in Fluid Solution. J Am Chem Soc. 1973; 95:1672–1673.

16. Tachikawa H, Bard AJ. Electrogenerated Chemiluminescence. Effect of a Magnetic Field on Delayed Fluorescence and Ecl of Several Systems Involving Excimers or Exciplexes. Chem Phys Lett. 1974; 26:568–573.

17. Santhana KSV. Magnetic Field Effect on Electrochemiluminescence of Carbazole. Can J Chem. 1971; 49:3577–3578.

18. Singh-Rachford TN, Castellano FN. Photon Upconversion Based on Sensitized Triplet-Triplet Annihilation. Coordin Chem Rev. 2010; 254:2560–2573.

19. Simon YC, Weder C. Low-power Photon Upconversion through Triplet-Triplet Annihilation in Polymers. J Mater Chem. 2012; 22:20817–20830.

20. Zhao JZ, Ji SM, Guo HM. Triplet-Triplet Annihilation Based Upconversion: from Triplet Sensitizers and Triplet Acceptors to Upconversion Quantum Yields. Rsc Adv. 2011; 1:937–950.

21. Baluschev S, Yakutkin V, Miteva T, Avlasevich Y, Chernov S, Aleshchenkov S, Nelles G, Cheprakov A, Yasuda A, Mullen K, Wegner G. Blue-green Upconversion: Noncoherent Excitation by NIR Light. Angew Chem Int Edit. 2007; 46:7693–7696.

22. Baluschev S, Yakutkin V, Miteva T, Wegner G, Roberts T, Nelles G, Yasuda A, Chernov S, Aleshchenkov S, Cheprakov A. A General Approach for Non-coherently Excited Annihilation Up-conversion: Transforming the Solar Spectrum. New J Phys. 2008; 10:013007.

23. Baluschev S, Yakutkin V, Wegner G, Miteva T, Nelles G, Yasuda A, Chernov S, Aleshchenkov S, Cheprakov A. Upconversion with Ultrabroad Excitation Band: Simultaneous use of Two Sensitizers. Appl Phys Lett. 2007; 90:181103.

24. Singh-Rachford TN, Castellano FN. Triplet Sensitized Red-to-Blue Photon Upconversion. J Phys Chem Lett. 2010; 1:195–200.

25. Singh-Rachford TN, Nayak A, Muro-Small ML, Goeb S, Therien MJ, Castellano FN. Supermolecular-Chromophore-Sensitized Near-Infrared-to-Visible Photon Upconversion. J Am Chem Soc. 2010; 132:14203–14211. [PubMed: 20828165]

26. Mezyk J, Tubino R, Monguzzi A, Mech A, Meinardi F. Effect of an External Magnetic Field on the Upconversion Photoluminescence of Organic Films: The Role of Disorder in Triplet-Triplet Annihilation. Phys Rev Lett. 2009; 102:087404. [PubMed: 19257785]

27. Piland GB, Burdett JJ, Kurunthu D, Bardeen CJ. Magnetic Field Effects on Singlet Fission and Fluorescence Decay Dynamics in Amorphous Rubrene. J Phys Chem C. 2013; 117:1224–1236.

28. Wohnhaas C, Turshatov A, Mailander V, Lorenz S, Baluschev S, Miteva T, Landfester K. Annihilation Upconversion in Cells by Embedding the Dye System in Polymeric Nanocapsules. Macromol Biosci. 2011; 11:772–778. [PubMed: 21384551]

29. Eastwood D, Gouterman M. Porphyrins. XVIII. Luminescence of (Co), (Ni), Pd, Pt Complexes. J Mol Spectrosc. 1970; 35:359–375.

30. Kobayashi T, Straub KD, Rentzepis PM. Energy Relaxation Mechanism in Ni(II), Pd(II), Pt(II) and Zn(II) Porphyrins. Photochem Photobiol. 1979; 29:925–931.

31. Suna A. Kinematics of Exciton-Exciton Annihilation in Molecular Crystals. Phys Rev B. 1970; 1:1716–1739.

32. Atkins PW, Evans GT. Magnetic-Field Effects on Chemiluminescent Fluid Solutions. Mol Phys. 1975; 29:921–935.

33. Finikova OS, Cheprakov AV, Beletskaya IP, Carroll PJ, Vinogradov SA. Novel versatile synthesis of substituted tetrabenzoporphyrins. J Org Chem. 2004; 69:522–535. [PubMed: 14725469]

34. Finikova OS, Cheprakov AV, Vinogradov SA. Synthesis and Luminescence of Soluble meso-Unsubstituted Tetrabenzo- and Tetranaphtho[2,3]porphyrins. J Org Chem. 2005; 70:9562–9572. [PubMed: 16268634]

35. Cheprakov AV, Filatov MA. The Dihydroisoindole Approach to Linearly Annelated -Extended Porphyrins. J Porphyr Phthalocya. 2009; 13:291–303.

36. Vinogradov SA, Wilson DF. Metallotetrabenzoporphyrins – New Phosphorescent Probes for Oxygen Measurements. J Chem Soc Perk Trans II. 1995:103–111.

37. Aartsma TJ, Gouterman M, Jochum C, Kwiram AL, Pepich BV, Williams LD. Porphyrins. 43. Triplet Sublevel Emission of Platinum Tetrabenzoporphyrin by Spectro-Thermal Principal Component Decomposition. J Am Chem Soc. 1982; 104:6278–6283.

38. Clarke RH, Hochstrasser RM. Location and Assignment of Lowest Triplet State of Perylene. J Mol Spectrosc. 1969; 32:309–319.

39. Esipova TV, Karagodov A, Miller J, Wilson DF, Busch TM, Vinogradov SA. Two New "Protected" Oxyphors for Biological Oximetry: Properties and Application in Tumor Imaging. Anal Chem. 2011; 83:8756–8765. [PubMed: 21961699]

40. Borisov SM, Larndorfer C, Klimant I. Triplet-Triplet Annihilation-Based Anti-Stokes Oxygen Sensing Materials with a Very Broad Dynamic Range. Adv Func Mat. 2012; 22:4360–4368.

41. Kubin RF, Fletcher AN. Fluorescence Quantum Yields of Some Rhodamine Dyes. J Lumin. 1982; 27:455–462.

42. Parker CA, Joyce TA. Formation Efficiency and Energy of Perylene Triplet. Chem Commun. 1966:108–109.

43. Whited MT, Djurovich PI, Roberts ST, Durrell AC, Schlenker CW, Bradforth SE, Thompson ME. Singlet and Triplet Excitation Management in a Bichromophoric Near-Infrared-Phosphorescent BODIPY-Benzoporphyrin Platinum Complex. J Am Chem Soc. 2011; 133:88–96. [PubMed: 21142032]

44. Mani T, Niedzwiedzki DM, Vinogradov SA. Generation of Phosphorescent Triplet States via Photoinduced Electron Transfer: Energy and Electron Transfer Dynamics in Pt porphyrin-Rhodamine B dyads. J Phys Chem A. 2012; 116:3598–610. [PubMed: 22400988]

45. Elsayed MA, Tinti DS, Yee EM. Conservation of Spin Direction and Production of Spin Alignment in Triplet-Triplet Energy Transfer. J Chem Phys. 1969; 51:5721–5723.

46. Clarke RH. Magnetic resonance studies of optical spin polarization in triplet state anthracene. Chem Phys Lett. 1970; 6:413–416.

47. Imamura T, Onitsuka O, Murai H, Obi K. Conservation of Spin Polarization during Triplet Triplet Energy-Transfer in Low-Temperature Matrices. J Phys Chem. 1984; 88:4028–4031.

48. Vandijk N, Noort M, Voelker S, Canters GW, Van der Waals JH. Zeeman Experiments on the $^3E_u$-$^1A_g$ Transition of Platinum Porphin in an Normal-Alkane Single-Crystal at 4.2 K. Chem Phys Lett. 1980; 71:415–423.

49. Vanderpoel WAJA, Nuijs AM, Van der Waals JH. Electron-Spin-Resonance in the $^4E_u$ State of Copper Porphine the $^3E_u$ State of Platinum Porphine in Normal-Octane Normal-Decane Crystals. J Phys Chem. 1986; 90:1537–1540.

50. Steren CA, Vanwilligen H, Dinse KP. Spin Dynamics of C-60 Triplets. J Phys Chem. 1994; 98:7464–7469.

51. Hirota N, Yamauchi S. Short-lived Excited Triplet States Studied by Time-Resolved EPR Spectroscopy. J Photoch Photobiol C. 2003; 4:109–124.

52. Iwasaki Y, Maeda K, Murai H. Time-domain Observation of External Magnetic Field Effects on the Delayed Fluorescence of N,N,N ,N -Tetramethyl-1,4-phenylenediamine in Alcoholic Solution. J Phys Chem. 2001; 105:2961–2966.

53. Jiang Y, Blanchard GJ. Rotational Diffusion Dynamics of Perylene in N-Alkanes – Observation of a Solvent Length-Dependent Change of Boundary-Condition. J Phys Chem. 1994; 98:6436–6440.

54. Lifshitz E, Kaplan A, Ehrenfreund E, Meissner D. Optically Detected Magnetic Resonance as a Tool to Study the Morphology of Perylene-derivative Thin Film. Chem Phys Lett. 1999; 300:626–632.

55. Jas GS, Larson EJ, Johnson CK, Kuczera K. Microscopic Details of Rotational Diffusion of Perylene in Organic Solvents: Molecular Dynamics Simulation and Experiment vs Debye-Stokes-Einstein Theory. J Phys Chem. 2000; 104:9841–9852.
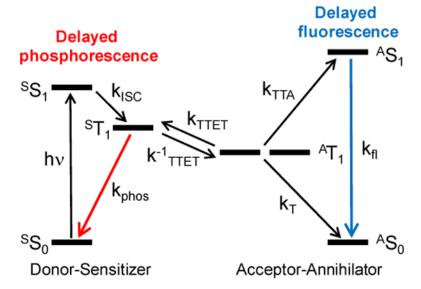
**Figure 1.**
Energy diagram associated with sensitized triplet-triplet annihilation.
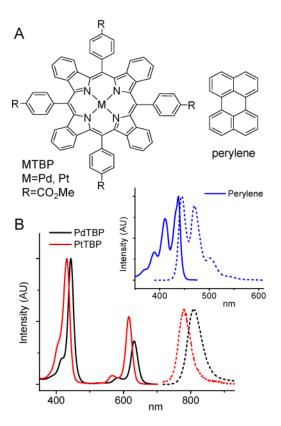
**Figure 2.**
(A) Molecular structures of the sensitizers (PtTBP and PdTBP) and the acceptor (perylene) used in this work. (B) Absorption (solid line) and emission (dashed line) spectra of the chromophores.
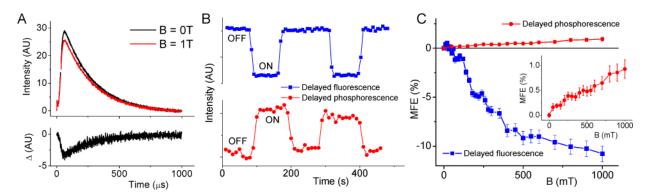
**Figure 3.**
(A) Time courses of delayed fluorescence of perylene in PdTBP/perylene system ([PdTBP]~5 µM, [perylene]~100 µM) in the absence and presence of magnetic field (B=1T) – upper graph; time course of the difference between the two signals – lower graph. (B) Changes in perylene delayed fluorescence and PdTBP delayed phosphorescence with application of magnetic field (B=1T). (C) MARY curves for delayed fluorescence and delayed phosphorescence (inset) in PdTBP/perylene mixtures. Delayed fluorescence: [PdTBP]~5 µM, [perylene]~100 µM. Delayed phosphorescence: [PdTBP]~5 µM, [perylene]~1 mM.
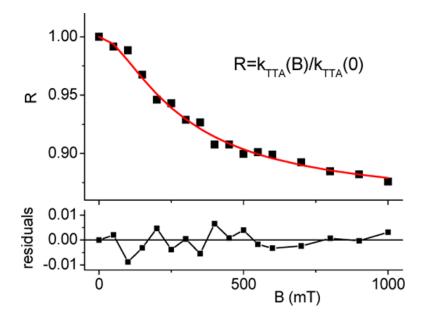
**Figure 4.**
Ratio of rate constants ($k_{TTA}$) as a function of magnetic field. The solid line shows the fit to Eq. 4. Experimental conditions: [PdTBP]~5 μM, [perylene]~1 mM.

**Table 1**

MFE on delayed emission in systems containing MTBP's as donors and perylene as acceptor.

| Donor | Acceptor | MFE (%)[a] | |
|---|---|---|---|
| | | Delayed fluorescence[b] | Delayed phosphorescence[c] |
| PtTBP | perlyene | −9.5 ± 0.2 | 1.2 ± 0.2 |
| PdTBP | | −10.8 ± 0.8 | 0.9 ± 0.2 |

[a]MFE(%)=100×[Y(B)−Y(0)]/Y(0), where Y(B) and Y(0) are the integrated intensities at B=1T and in zero-field, respectively

[b][Donor]=~5 μM, [Acceptor]=~100 μM

[c][Donor]=~5 μM [Acceptor]=~1 mM.