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Dedicated to the 90th anniversary
of Zainulla M. Muldakhmetov

Boris F. Minaev[1, 2]

[1]*Department of Physics and Astronomy, Uppsala University, Sweden;*
[2]*Department of Chemistry and Nanomaterials Science, Bohdan Khmelnytsky National University, Cherkasy, Ukraine*
(Author's e-mail: bfmin43@ukr.net)

Spin Catalysis in Photochemical Reactions and Its Applications to Quantum Information Nanotechnology

Chemistry as a science about spin and electric charge of micro particles which provide driving forces of atomic interactions and molecular structure transformations fits pretty well to the modern Quantum Information Science (QIS) requirements. Today's computers operate only electric current signals in the semiconductor networks but the electron-spin properties are not exploited in a large extend. Spintronics provides spin-polarized currents and manipulates magnetic spin interactions; it uses mostly solid state chemistry of heavy elements. But a rich organic chemistry of solvents and fin films offers a great potential for molecular electronics and quantum computing. Photo-excited organic complexes of the "chromophore–radical" type provide good promise for many technological applications in molecular spintronics and electronics, including QIS technology. The doublet state photo excitation of stable organic radical being delocalized onto the linked anthracene molecule within picoseconds and subsequently evolved into a quartet state for big radicals (a pure high spin state) of the mixed radical-triplet character presents a sensible spin-optical interface for qubit in quantum computing. This high-spin state is coherently addressable with EPR microwaves even at room temperature, with the optical read-out induced by intersystem crossing (ISC) to emissive triplet state. Such integration of radical luminescence and high-spin states EPR provides the organic materials involvement into emerging QIS technologies.

Keywords: spin catalysis, quantum information science, high-spin states, radical luminescence, quantum nanotechnology, spintronics.

Introduction

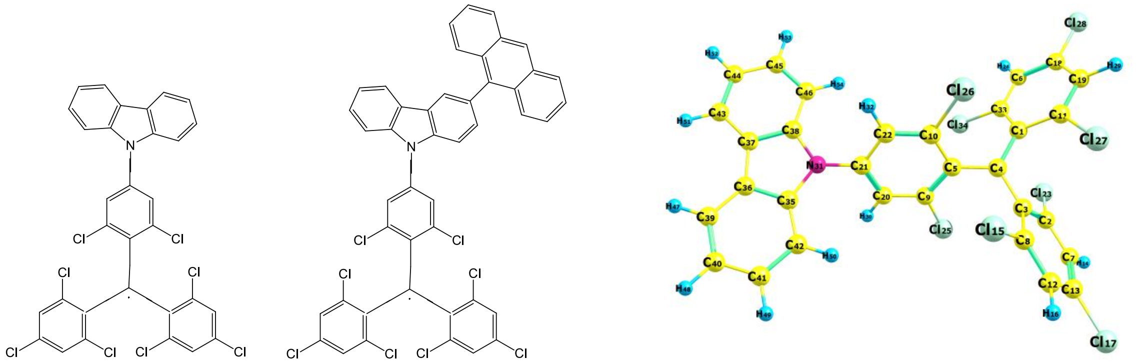
Molecular electronics and nano-photonics represent versatile platforms for information storage, sensing, encryption, including quantum bit science applications [1–15]. Quantum information science researches are the leading technology forces of XXI century. Quantum teleportation, quantum entanglement and quantum computer manufacturing strongly depend on the comprehensive knowledge and understanding of quantum physics and chemical nano-engineering of particular functional materials. Some IT companies (like Google and IBM) have invested great money since 2010 into hardware research of quantum computer (QC) and recently reached significant progress in the QC manufacturing and quantum cryptography [1] (the late devices are now commercially available). Quantum cipherization will substitute the widely used ciphers like RSA and ECC [6]. New functional materials based on π–conjugation of organic π–radical and chromophore represent sensible spin-optical interface to utilize unique quantum resources of organic materials. Eighty years ago, academic A.N. Terenin had opened the door to utilize such quantum resources of the triplet excited state of organic chromophores explaining their phosphorescence in solid solvents [15]. Almost simultaneously, academic E.K. Zavoisky had discovered another fundamental physical phenomenon — electron paramagnetic resonance (EPR) for studies of electron spin distribution in radicals [2]. Both discoveries provided a deep background for the spin chemistry and molecular spintronics development for the next century [1–15].

Main Part

Radicals with non-paired spins can be generated by photochemical reactions in organic solvents. Their recombination is a spin-sensitive process which depends on diffusion, concentration, intermolecular exchange and magnetic interactions [2, 3]. These radical pairs (RP) were exploited in chemically induced dynamic nuclear polarization (CIDNP) phenomena, electron spin polarization in EPR spectroscopy and in the external magnetic field effects (MFE) in radical recombination reactions [2–4] including O_2 activation by enzymes [5].

Academic Kev Minullinovich Salikhov, Director of the Zavoisky Physical-Technical Institute (who visited Karaganda State University many times and is a good friend of Zainulla Muldakhmetov) has proposed [3] that the third spin in the time-resolved ESR spectra of the light-induced radical pair (RP) can play an important role of the third observer and spin driver in the luminescent response of the whole three-radicals system. And such third observer could provide potential application in the so-called quantum teleportation, which is one of the modern technologies in the information transfer, cipherization, encryption, and in other researches of the quantum information science [6–14]. The authors of Ref. [11] synthesized the first organic system which displays simultaneously both strong luminescence and the near-unity generation quantum yield of the quartet (and quintet) excited states of high-spin multiplicity (HSM) produced by a link of radical with chromophore.

Though many stable radicals are non-luminescent [8], a new class of emissive radicals was synthesized recently that provides intense emission by spin-allowed electric dipole transitions within the doublet state manifold [15]. This class of available radicals quite rapidly expands their molecular structures and spans the whole visible region including a near IR wavelength range [15]. The best record efficiencies for organic light emitting diodes working in the deep-red and IR regions were recently obtained with the tris(2,4,6-trichlorophenyl)methyl radicals conjugated with carbazole moiety as an electron donor (Fig. 1A) [11, 15].



A *B* *C*

Figure 1. Chemical structure of the tris(2,4,6-trichlorophenyl)methyl radical (TTM) linked to carbazole: TTM-Cz (*A*); the common radical produced by TTM-Cz conjugation with the antracene chromophore (*B*) synthesized by Gorgon at el. [11]; the DFT optimized TTM-Cz radical (*C*)

Gorgon at el. [11] designed the energy resonance between emissive doublet and triplet levels, by covalently coupled tris(trichlorophenyl)methyl-carbazole (TTM-Cz) radical and anthracene (An) molecule (Fig. 1B); they observed the doublet excitation (D) delocalised to the linked anthracene within a picosecond lifetime being evolved subsequently to the pure HSM state of the mixed radical-triplet type at low energy (near 1.8 eV). These are quartet HSM state for the monoradical+acene system (TTM-Cz+An), and subsequently — quintet HSM state for the biradicaloid combination $(TTM\text{-}Cz)_2$+An [11]. The authors used impulse EPR scanning of these HSM states by microwaves at room temperature [11]. Presence of radical in combination with acene enhances the rate of intersystem crossing (ISC), which leads to the high An chromophore triplet states population. Gorgon et al. [11] were succeeding in experiments with coherently addressable by EPR signal of TTM-Cz radical with an optical phosphorescent read-out of anthracene 1B molecule in a dilute toluene solution (even at 295 K) being enabled by ISC to transfer into the emissive states [11]. In the biradical complex system (TTM-Cz)$_2$+An, on return to the ground singlet S_0 state the radical spins on either side of the anthracene molecule show strong spin correlation (though they were uncorrelated initially). This approach supports a high efficiency of initialisation, spin manipulations and simultaneously light-based read-out in the radical-An system at room temperature in dilute toluene solution [11]. Such integration of luminescence and HSM states [16] creates a robust chemical synthetic platform based on organic functional materials for emerging modern quantum computation technologies [10–14]. Further QIS technology development of HSM systems strongly depends on the capability to control the spin-magnetic properties of such materials, and requires comprehensive understanding of spin-orbit coupling impact on excited-state dynamics. Quantum chemical treatments of various spin effects based on radical interactions with the triplet excited states were considered in Karaganda State University as early as 45 years ago in the context of spin alignment and microwave induced optical phosphorescence detection [16, 18]. Combinations of the anthracene core with various carbazole moieties in fused heteroacenes were utilized in recent fabrication of highly luminous sky-blue organic light-emitting diodes [17] and their linking with radicals could be potentially interesting for HSM states generation [11–14]. Zainulla Muldakhmetov, as a founder of modern spectroscopy in the Central Kazakhstan region put forward new kinetics photochemical methods of optical-magnetic resonance, EPR, flash-photolysis and quantum-chemical approaches [18] which provide essential fundamental backgrounds for contemporary quantum cipherization, information transfer, integration of luminescence and high-spin states dynamics. All these efforts created an organic materials platform for emerging quantum information technologies [9–12, 18–21].

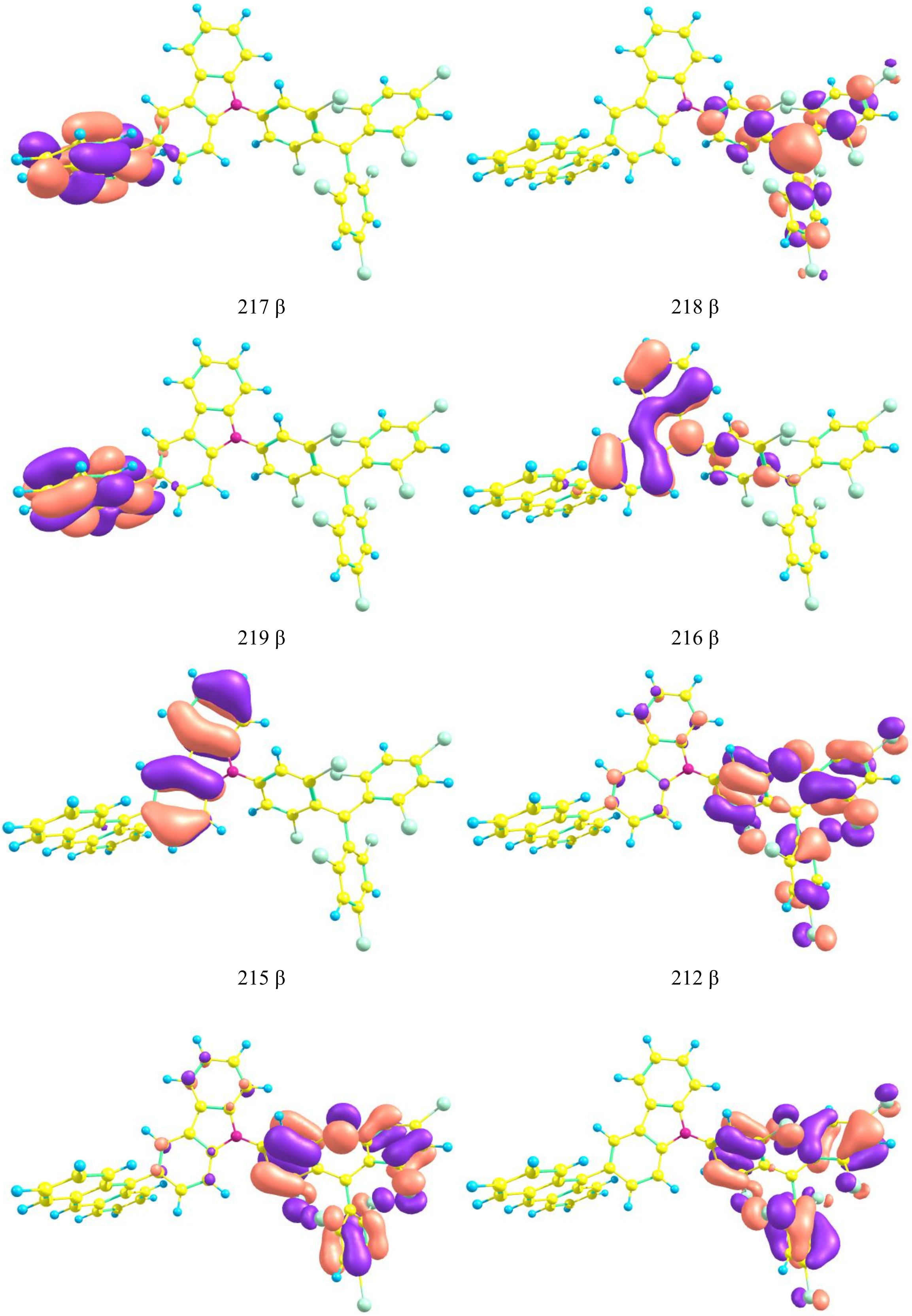
In the present work an attempt is made to illustrate the quantum chemical feature of the new systems on the ground of time dependent (TD) density functional theory (DFT) with the spin-UB3LYP functional. The results provide an assignment of the electronic absorption UV-vis spectrum of the common radical produced by TTM-Cz conjugation with the anthracene chrmophore synthesized by Gorgon et al. Figure 1B [11]. They are shown in Table. Figure 2 presents the frontier molecular orbitals (MOs) of this TTM-Cz-An radical.

All radicals (TTM, TTM-Cz and TTM-Cz-An) structures are optimized by DFT UB3LYP method and their IR spectra are analyzed in terms of normal vibrations; all frequencies of vibrational modes were found to be real. One can see in Figure 2 that the antracene chrmophore's MOs are almost independent from the electronic system of the TTM-Cz radical. Only the highest doubly occupied molecular orbitals (HOMO) (217β and 218α) and the next to the lowest unoccupied molecular orbital (LUMO+1) 219β have small admixtures at the place of conjugation between antracene chrmophore and the radical electronic system (Fig. 2).

Table

TD DFT calculation of the electronic absorption spectrum of the TTM-Cz-An radical and rotatory strengths (*R*) in CGS (10^{-40} erg esu cm/Gauss); *λ* — wavelength, *f* — oscillator strength

State	E (eV)	λ (nm)	f	Configuration state function	R_{XX}	R_{YY}	R_{ZZ}	R length
CT	1.570	790.9	0.0051	(217β→218β)	0.46	0.15	0.05	0.19
D_0T_1	1.769	700.1	10^{-6}	0.70(217β→219β)- -0.69(218α→219α)	0	0	0	0
D_1S_0	1.897	653.7	0.1030	0.98(216β→218β)	–7.81	4.43	–6.54	–3.30
D_3	2.284	542.8	0	(215β →218β)	0	0	0	0
D_4	2.660	466.1	0.0174	0.81(212β→218β)	–5.78	–22.3	–7.11	–11.5
D_5	2.764	448.4	0.0062	0.75 (210β→218β)	4.28	0	0	1.42
D_6	2.848	435.4	0	0.91(214β→218β)	0.36	0.12	0	0.14
D_7	2.899	427.6	0.0031	0.71(209β→218β) +0.44(208β→218β)	2.15	7.14	–26.3	–5.36
D_8	2.949	420.6	0.0027	0.68(207β→218β)- -0.28(217α→-220α)	–42.4	0.99	–11.8	–17.7
D_9	2.950	420.2	0.0039	+0.71(208β→218β)- 0.50(209β→218β)	–1.32	13.98	–53.3	–13.4



217 β

218 β

219 β

216 β

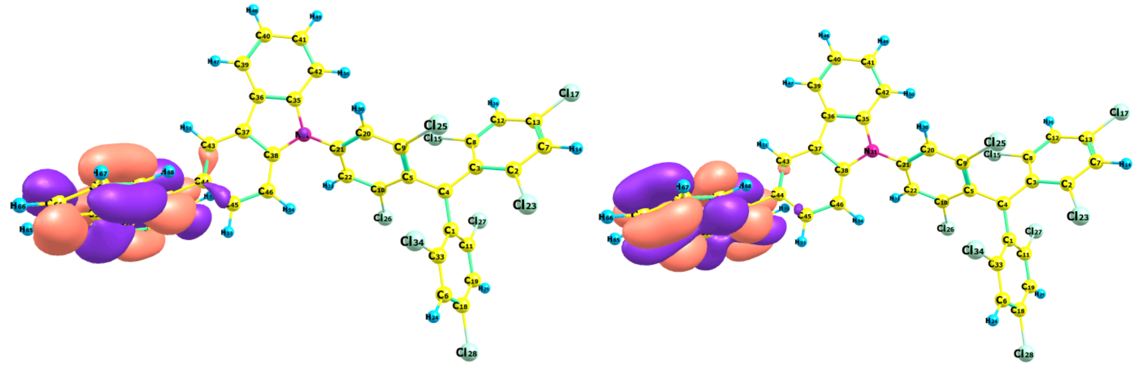
215 β

212 β

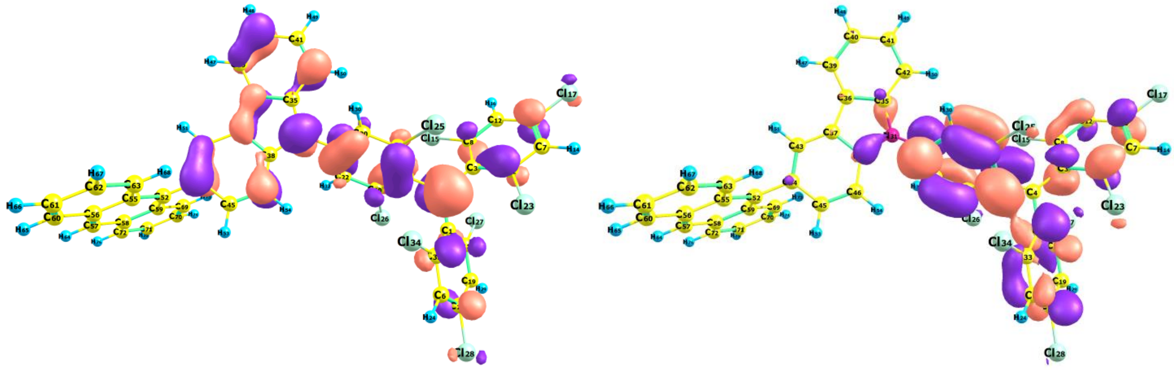
209 β

208 β

Figure 2*a*. Frontier molecular orbitals for β spins of the radical TTM-Cz-Anthracene depicted in Figure 1B



218 HOMO α 219 LUMO α



217 α 220 α

Figure 2*b*. Frontier molecular orbitals for α spins of the radical

According to our calculation, the first excited state of the whole radical corresponds to a pure charge transfer (CT) transition from anthracene to the TTM radical moiety 217β→218β (Fig. 2*a*). It produces a moderately intense absorption band ($f = 0.005$) with a maximum at 790 nm (Table). This result does not coincide with interpretation of Gorgon at el. [11], who believe that CT state is higher in energy than the first excited state of the TTM-Cz radical. Probably, our TD DFT calculation underestimates the CT state energy, but the rest assignments are in agreement with experiment [11]. The D_0S_0-D_0T_1 excitation in anthracene (1.769 eV) occurs below the first excited state in the TTM-Cz radical (1.897 eV); the late represents (216β→218β) transition with the largest intensity ($f = 0.103$; Table). This is almost pure doublet state (S^2 expectation value is 0.81 instead of 0.75 for S=1/2). The ground state D_0 has the S^2 expectation value equal to 0.77 and after spin annihilation we get 0.7504 value. The $D_0 – D_1$ transition represents a single electron excitation 216β→218β, that is an excitation in the TTM-Cz radical with a large portion of charge transfer from the carbazole moiety to the TTM radical (Fig. 2*a*). At the same time, the singly occupied molecular orbital (SOMO) 217α in the ground radical state D_0 represents the whole TTM-Cz radical (Fig. 2*b*), it is bearing one nonpaired α electron. It should be noted that the 218 β MO (which is a virtual analogous of SOMO) does not include contribution from the carbazole moiety (Fig. 2*a*). The spin density in the excited CT state (1.57 eV) represents mostly the An^+ cation radical of anthracene (217β) and minimal contribution from the carbazole moiety. The whole TTM-Cz-An radical is now transferred into the $(TTM)^-$ anion (218β) with an almost closed-shell electronic structure that is linked with the anthracene cation radical.

In order to understand comparison with the experimental spectra [11] we have to analyze absorption and luminescence of both radicals A and B shown in Figure 1. The TD DFT calculation results for the electronic absorption spectrum of the A radical (TTM-Cz) are presented in Table S1 **Supplementary Materials**. First, we need to compare $D_0 \rightarrow D_1$ transition in radical A with the $D_0S_0 \rightarrow D_1S_0$ absorption band in the composed B radical (TTM-Cz-An). The band $D_0 – D_1$ includes transition from the doubly occupied 171 MO (Fig. S1) to the singly occupied molecular orbital (SOMO) 172. This is the allowed long-axis polarized transition which embraces the whole TTM-Cz species; this is mostly $\pi \rightarrow \pi^*$ type excitation. Its analogous in the composed B radical (TTM-Cz-An) could be the 216α →217α transition (Fig. S1). In fact, the D_1S_0 state in the late radical B is presented by 216β→ 218β configuration and bears some CT character inside the A radical (Figure 1; TTM-Cz). The third excited state at 1.897 eV (654 nm) in the TTM-Cz-An radical represents the doublet state (Table). In the TTM-Cz radical (Fig. 1A) calculated by the same TD DFT method the first excited doublet state is at 1.875 eV (661 nm); thus, it is shifted to the red region in comparison with 1.897 eV excitation energy of the radical B. The second transition in the A radical is a charge transfer excitation from the carbazole moiety to the TTM radical.

In experiment [11] the light absorption with the wavelength higher than that for the first singlet-singlet S_0–S_1 transition in anthracene corresponds to the D_0S_0-D_1S_0 absorption band. This radical-excited state is close to the doublet D_0T_1 anthracene (T_1) excited state (Table). According to [11] a rapid doublet-doublet relaxation of radical excitation D_1S_0 to the coupled anthracene D_0T_1 state proceeds within a few picoseconds. This fast rate is possible since the total spin is conserved during such "doublet radical → triplet molecule" energy transfer. Subsequently, the doublet $^2[D_0T_1]$ exciton undergoes intersystem crossing (ISC) transition to the anthracene–excited quartet state $^4[D_0T_1]$. The rate of such ISC depends on spin-orbit coupling (SOC) matrix element (ME). The spatial (orbital) part of the doublet $^2[D_0T_1]$ and quartet $^4[D_0T_1]$ wave functions are very close; thus, the SOC ME is expected to be negligible [11]. In fact, account of all α and β MOs differences leads to prediction that this direct SOC matrix element is not small. We have estimated it within the PM3 approximation accounting the spin-restricted Hartree-Foch method with the limited configuration interaction [16–19] to be equal 0.237 cm^{-1}. Nevertheless, the square of SOC ME which determines the ISC rate is really small and cannot compete with other $^2[D_0T_1]$ doublet state relaxation processes. Thus, the direct ISC seems impossible to generate high yields of the quartet $^4[D_0T_1]$ state at the nanoseconds timescales in agreement with the observed dynamics of the composed TTM-Cz-An radical luminescence.

The authors of [11] proposed that the CT state (in Table it corresponds to 217β→218β excitation) could be close in energy to both $^{4,2}[D_0T_1]$ states of the anthracene-excitonic type. Though our TD DFT calculation puts the CT state too low in energy, in reality it still could be an intermediate in the $^2[D_0T_1]$ -$^4[D_0T_1]$ relaxation. The CT state accessibility could assist ISC process to the quartet state via SOC, which must be definitely higher for the states of different orbital character (Table, Fig. 2). The CT state can be easily produced (according to [11]) from the $^2[D_0T_1]$ doublet following spin-conserving electron transfer from locally excited anthracene into the single vacancy of radical; that is, from the LUMO 219α of anthracene to the SOMO 217α of TTN-Cz radical (Fig. 2b). If the ISC transition occurs during the reverse electron-transfer, then the spin flip and the quartet $^4[D_0T_1]$ state can be formed. The authors of [11] have proposed that such forward mechanism could be near-barrierless and could explain their experimental observation of a high quantum yield of the quartet state at all studied conditions in a great interval from 20 K till room temperatures. The late was measured from the $D_1 \rightarrow D_0$ luminescence quantum efficiency of radical B (Fig. 1) together with the triplet $^2[D_0T_1]$ state yield extracted from the measured transient optical absorption. For the TTM-Cz-An radical in the toluene solutions at room temperature the quartet state yield was about 73 %. [11]. Thus, combining PL spectroscopy, EPR, and optical detection of magnetic resonance, the authors of [11] show a possibility to generate the pure high-spin states in organic molecules, to manipulate them, and then to read them out by radical luminescence at ambient condition. Taking into account the correction for the low CT state energy, we try here to support this discovery, which is quite important for the modern quantum information science.

Conclusions

It was shown recently [11] that synthetic chemical tuning of poly-radical molecular structures opens new ways to design the coupled high-multiplicity spin systems, which could be addressed by light of chosen wavelengths range. The tria(trichlorophenyl)methyl-carbazole (TTM-Cz) radical covalently coupled with anthracene was studied in the present work in order to explain how the doublet excitation delocalized to the linked anthracene during a picosecond lifetime can be evolved into the high-multiplicity (quartet) spin state of the mixed radical-triplet type at low excitation energy in the visible region. High-spin quartet (and quintet) states are able to produce the dense architecture with multiple qubits distributed within the single manifold of spin sublevels. These multilevel qubits offer great advantages in the quantum information science and quantum computing.

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Information about author*

Minaev, Boris Filippovich (*corresponding author*) — Doctor Of Chemical Sciences, Professor, Department of Physics and Astronomy, Uppsala University, SE-752 37, Uppsala, Sweden; Department of Chemistry and Nanomaterials Science, Bohdan Khmelnytsky National University, 18031, Cherkasy, Ukraine; e-mail: bfmin43@ukr.net; https://orcid.org/0000-0002-9165-9649;

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*The author's name is presented in the order: *Last Name, First and Middle Names*