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**QUANTUM CHEMICAL CALCULATIONS
OF THE ACRIDONE-2,2'-DINAPHTHYLAMINE DERIVATIVE
AS AN EMITTER FOR OLED WITH THE THERMALLY-ACTIVATED
DELAYED FLUORESCENCE**

Electronic structure of the recently synthesized molecule in the ground and excited states of the N-methylacridone derivative is calculated by the PM3 self-consistent field method with geometry optimization. Calculations show that the molecule is non-symmetric in the ground state and a strong asymmetric distortion is predicted for the excited triplet state. This explains a long vibrational progression in the emission spectra and the low external quantum efficiency of the fabricated organic light emitting diode based on this compound.

Keywords: thermally-activated delayed fluorescence, vibronic displacement, acridones, OLED architecture and interface, spin-orbit coupling, self-consistent field.

1. Introduction

Organic materials in the form of polymers, nano-clusters and small molecules can be usually treated as semiconductors. Because of the presence of variable conjugated C=C and C=X bonds (X represent mainly N and O as heteroatoms in the conjugation chain), organic semiconductors typically have intense absorption and emission spectra in UV and visible range. In principle, they are typical insulators since the charge carriers are provided by electrode injection or doping [1,2]. In comparison with GaAs these organic materials have considerable advantages in nanoelectronics because of easy tuning by modification of chemical structure, mechanical flexibility and low-cost fabrication [2]. Thus, organic semiconductors are widely implemented as a useful alternative to inorganic materials in light-emitting diodes, field-effect transistors and other devices of opto-electronics. They are especially suitable for flat displays as well as lighting sources in the form of organic light-emitting diode (OLED). The search for new efficient organic materials for OLEDs is still a growing challenge in organic synthesis, photophysics and quantum theory [2]. This paper is devoted to theoretical calculation and spectral analysis of synthetic and photophysical results obtained in Ref. [1] aimed to provide efficient OLED fabrication.

2. Results and discussion

The authors of Ref. [1] have presented recently an interesting synthesis of A-D-A type compound in order to implement it as a thermally-activated delayed fluorescence (TADF) material in OLEDs. Acridone, known also as acridine-9-one, was used as a starting reactant together with 2,2'-dinaphthylamine [1]. At the first glance, the synthesized compound **1** seems to be a symmetric molecule if the dihedral angle CCNC between two naphthalene moieties would be equal each other. In this case, the N-O axis could be an axis of the C_2 type and determine the reflection plane. The authors of Ref. [1] have not presented neither structural analysis of the new compound **1** nor any quantum chemical calculations of this molecule.

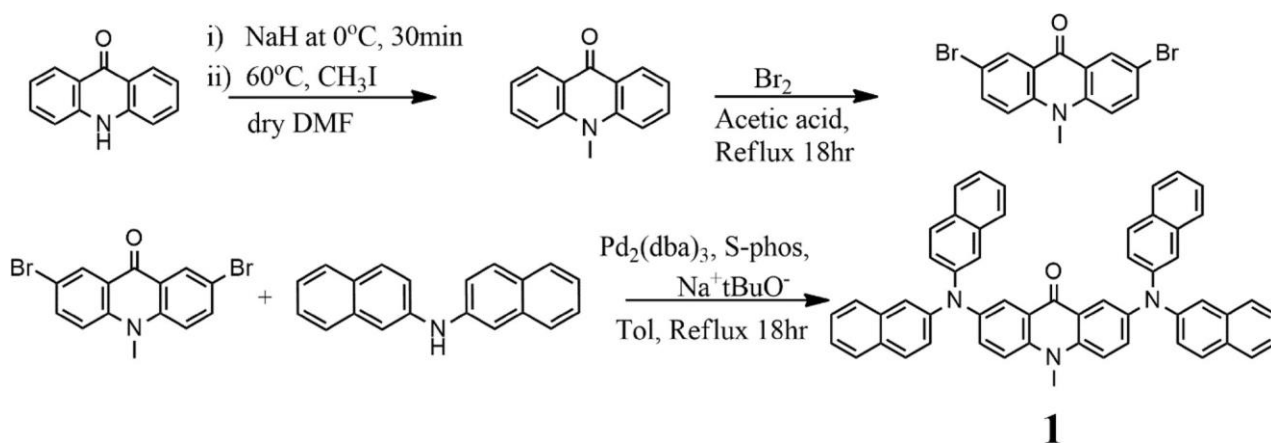


Fig. 1. The scheme of synthesis of compound **1** of the A-D-A type presented in Ref. [1] as a thermally-activated delayed fluorescence (TADF) material.

Рис. 1. Схема синтезу сполуки **1** типу А-D-A, представлена в посиланні [1] у вигляді термічно-активованого матеріалу із затримкою флуоресценції.

Being interesting in the general OLED architecture and its interface arrangement [2,3] we have performed semiempirical self-consistent field (SCF) calculations of the structure and spectral properties of compound **1** in the framework of PM3 approach [4–5]. The scheme of synthesis of acridone (acceptor) - naphthylamine (donor) derivative, denoted as compound **1** and being presented by the authors of Ref. [1], is shown in Fig. 1. They have measured the absorption and emission spectra of compound **1** and kinetics of TADF depending on solvent and aggregation properties in solid films. The compound **1** is a fluorescent molecule as a typical organic chromophore with the lowest excited singlet (S_1) state of $\pi\pi^*$ type; it emits in the green region with 560 nm at the maximum of fluorescence band in acetonitrile, Fig. 2. (A) [1]. Thus, the energy gap between the ground singlet state (S_0) and the lowest excited S_1 state is estimated to be 2.21 eV. Our calculation with PM3 method of configuration interaction (CI) for 140 single-excited state functions provides for the vertical S_0 - S_1 transition much higher energy excitation equals to 3.85 eV, Table 1. The transition is very intense with the calculated oscillator strength $f = 0.929$ being in a good agreement with experimental absorption and excitation spectrum (Fig. 2a).

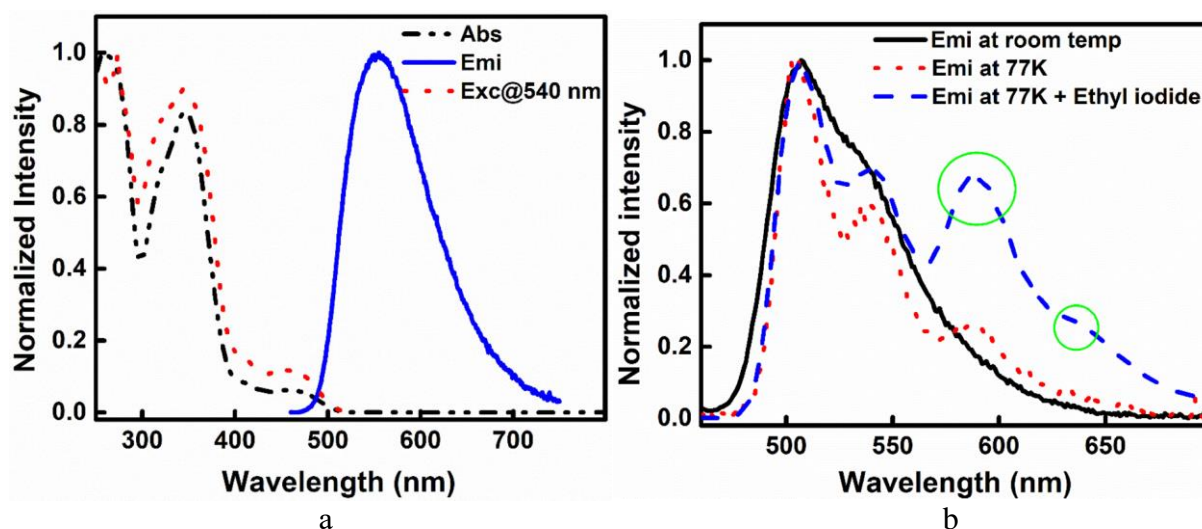


Fig. 2. (a). Absorption (dash-dotted black curve), emission (blue) and excitation (dotted curve) spectra of compound **1** in solvent (acetonitrile) [1]. Excitation spectrum is induced by 540 nm. (b). Emission spectra in methyl tetrahydrofuran solvent at 297 K (black curve), at 77 K (dotted curve) and at 77K with addition of ethyl iodide (10% v/v) in the solvent (dashed curve with circles).

Рис. 2. (а). Спектри поглинання (пунктирна чорна крива), випромінювання (синій) та збудження (пунктирна крива) сполуки **1** у розчиннику (ацетонітрил) [1]. Спектр збудження індукується 540 нм. (б). Спектри випромінювання в розчиннику метилтетрагідрофурану при 297 К (чорна крива), при 77 К (пунктирна крива) та при 77 К з додаванням етильїодиду (10% об. / Об.) у розчиннику (пунктирна крива з колами).

The authors of Ref. [1] have estimated the energy gap between the charge-transfer singlet and triplet states as being found 0.3 eV. Such small energy gap S_1-T_1 was considered as the reason for TADF observation, since the small ΔE_{S-T} gap is usually an important criterium for TADF emission to take place in a molecule [2]. The authors have studied the detailed photophysics, presented in Fig. 2. (B) and the transient lifetime measurements at different temperature and solvents. They observed a large increase in fluorescence lifetime on purging with nitrogen, as being compared with emission in the air-saturated solution [1]. This indicates an involvement of the triplet T_1 state in the observed emission and authors [1] ascribed it to TADF effect. It is difficult to understand why the authors of Ref. [1] always discuss an emission at 550 nm, though such particular wavelength is not seen in Fig. 2 as any particular feature in the emission spectra. The emission of compound **1** in methyl THF liquid solvent at room temperature and in solid glass at 77K indicates the clear vibronic progression. The observed delay of 0.07 ms [1] corresponds to the delayed fluorescence of the E-type activated at room temperature in air-saturated acetonitrile [3]. The lifetime of TADF was found to be 0.176 ms in nitrogen purged solvent [1]. Applications of TADF materials in OLED technology has received big attention recently [2,3] since such materials utilise the triplet excitons which helps in increasing internal quantum efficiency (IQE) of OLED device. Air-saturated OLED based on compound **1** in emitting layer was fabricated and its intensity was found to be as high as 17,000 Cd/m² at the current 25 mA/cm² [1] being comparable to the other known OLEDs using the TADF phenomena [2]. Our quantum-chemical calculations shed a new light on results of Ref. [1] and provide their alternative interpretation.

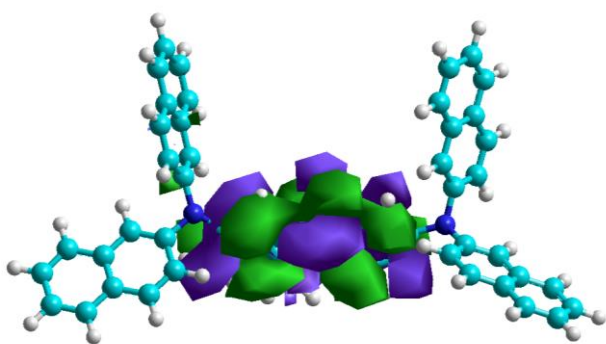


Fig. 3. LUMO (138 MO) of compound 1.

Рис. 3. LUMO (138 MO) сполуки 1.

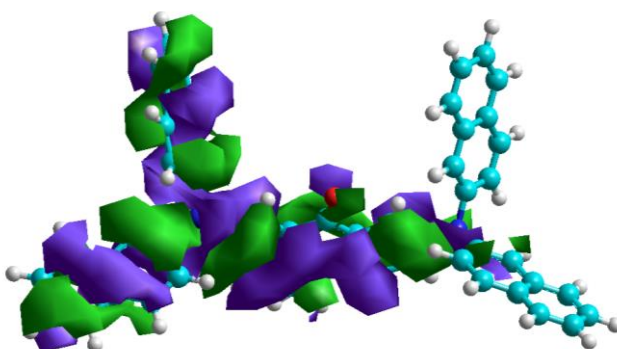


Fig. 4. HOMO (137 MO) of compound 1.

Рис. 4. HOMO (137 MO) сполуки 1.

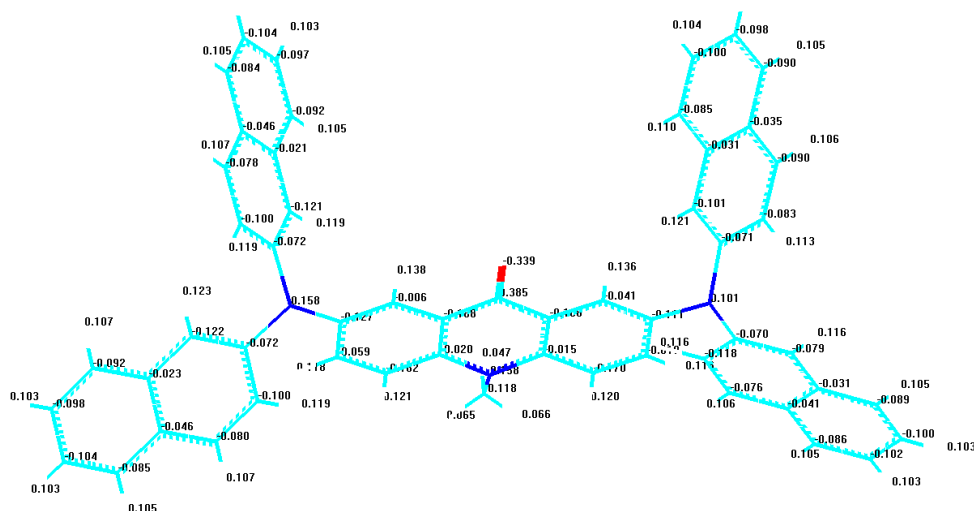


Fig. 5. Atomic charge distribution in the acridone dinaphthylamine derivative 1 ground state.

Рис. 5. Розподіл атомного заряду в основному стані похідного акридону динафтиламіну.

The PM3 geometry optimization in the ground singlet state (S_0) shows that the molecule is non-symmetrical. The highest occupied molecular orbital (HOMO) clearly demonstrates the absence of the left-right symmetry (Fig. 4), though the lowest unoccupied molecular orbital (LUMO) is found to be more symmetrical (Fig. 3). The atomic charge distribution (in the electron charge units) in Fig. 5 indicates the electronic densities in the left and right part of acridone moiety are different including nitrogen atom links with 2,2'-dinaphthylamine moieties. Both nitrogen atoms have positive charges as well as the whole dinaphthylamine parts; thus it is difficult to consider them as acceptors. At the same time, the acridone moiety bears some excess of negative charges and the whole structure could be treated better as the D–A–D type of compound. The left and right N atoms have very different charges (0.158 and 0.101, respectively). The same inequality concerns the N–C bond lengths. In the left part they are shorter by about 0.01 Å. Geometry optimization of the triplet excited T_1 state by the spin unrestricted Hartree-Fock (UHF) method predicts much more distortion in the left-right symmetry. Now the left N–C link is equal 1.41 Å and the right link is 1.47 Å. Similar difference in distortion of the left and right acridone rings can be mentioned in favor of the anti quinoid structure in the left ring. Not very much distortion is observed in the naphthalene rings. These peculiarities of the optimized geometry in the T_1 excited state are consistent with the spin density distribution (Fig. 6) which is characterized by strong asymmetry.

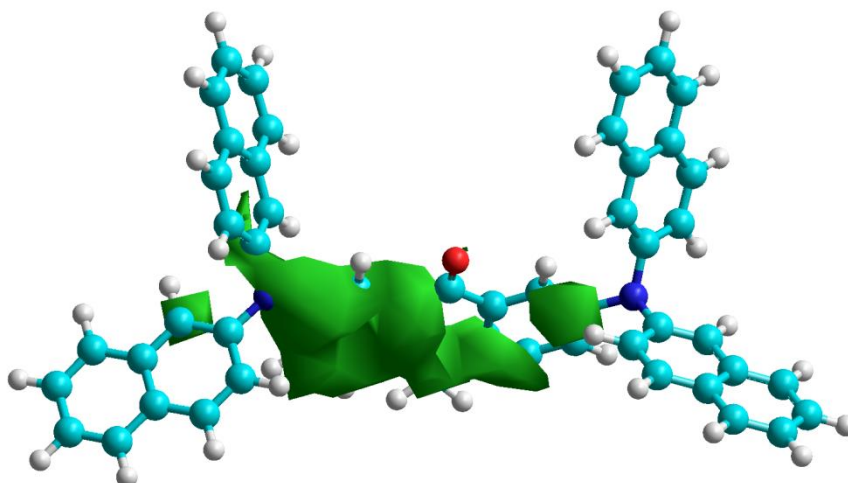


Fig. 6. Spin density distribution in the triplet excited state at the optimized T_1 geometry.
Рис. 6. Розподіл густини спіна в триплетному збудженому стані за оптимізованої геометрії T_1 .

One can see from Fig. 6 that the spin density in the triplet excited T_1 state is strongly localized in the left part of the acridone moiety. These results of geometry optimization by the UHF method for the triplet excited T_1 state are rather different from the vertical CI calculation at the S_0 optimized structure. The UHF method gives the 0-0 transition energy for ΔE_{S-T} gap equal to 1.42 eV; much lower than 2.99 eV for the vertical $S_0 \rightarrow T_1$ transition in Table 1. Even the orbital nature of the T_1 state is different as being predicted by these two methods.

Table 1.

The vertical absorption spectrum obtained by CI calculation at the S_0 optimized geometry; f – oscillator strength (dimensionless), λ – wavelength, μ – dipole moment.

Таблиця 1.

Вертикальний спектр поглинання, отриманий розрахунком CI за оптимізованої геометрії S_0 ; f - сила осцилятора (безрозмірна), λ - довжина хвилі, μ - дипольний момент.

Excited state	E, eV	λ , nm	f	Wave function	μ , Debye
T_1	2.99	414.7	0	[134→141]	3.4
S_1	3.85	321.6	0.929	137→140	4.1
S_2	4.06	305.5	0.166	137→139	5.3
S_3	4.09	303.0	0.422	137→138	7.0
S_4	4.30	288.0	0.362	135→138	4.7
S_6	4.51	274.8	0.751	134→141	4.1
S_9	5.03	246.4	0.799	133→135	7.7

Excitation (134→141) of the T_1 state in Table 1 corresponds to molecular orbitals localized in the right side of the molecule **1**. Thus, geometry optimization by the UHF method provides another triplet state as the first excited T_1 one. The results of Table 1 provide a good agreement with absorption spectrum given in Fig. 2a. The weak and wide violet absorption band at 400-440 nm, Fig. 2a) corresponds to spin-forbidden vertical $S_0 \rightarrow T_1$ transition at 414.7 nm (Table 1). The unplanar structure of the whole molecule produces σ - π mixture of orbitals localized in the region of C-N links between chromophore, which is typical for HOMO 137 (Fig. 4) and other orbitals like 134-141. Such σ - π mixing is responsible for increase of spin-orbit coupling (SOC) between S and T states, which removes the spin prohibition for $S_0 \rightarrow T_1$ transition [2]. This first absorption band is observed in the visible region as a wide feature; the width can be explained by a large geometry distortion upon $S_0 \rightarrow T_1$ excitation. It is important that the first $S_0 \rightarrow S_1$ transition is predicted by CI calculation as

the most intense absorption band ($f=0.929$, Table 1); thus, the weak wide feature at 414 nm can be ascribed only to $S_0 \rightarrow T_1$ transition. The twist at 305-303 nm, Fig. 2 (A), is also well reproduced by our calculation (Table 1) as well as intense UV absorption at wavelengths <275 nm.

The $S_0 \rightarrow S_3$ transition at 303 nm represents HOMO-LUMO excitation (137 \rightarrow 138), Table 1. From Figures 3 and 4 one can see that it includes a big portion of charge transfer from the left dinaphthylamine moiety to the central acridone part with simultaneous internal excitation of the electronic cloud in the center. That is why the S_3 state has a relatively large dipole moment (7 D), while the ground S_0 state shows only 3.55 D. Many other excited states have rather similar dipole moments. Thus, it is difficult to assign them to charge-transfer states. In particular, the fluorescent S_1 state have the dipole moment not very different from the ground state. Upon geometry optimization the dipole moments of the S_1 and T_1 states are only slightly increased (up to 3.7 D).

After $S_0 \rightarrow S_1$ excitation the molecule undergoes a fast and strong geometry distortion to the S_1 state equilibrium; thus, its fluorescence is shifted to the red region and corresponds mainly to the 0-0 transition in emission. Equilibrium of the S_1 state is distorted similar to the triplet one. This explains the wide form of emission band with a maximum at about 560 nm in acetonitrile, Fig. 2a. The polar solvent enhances the distorted bond lengths because of their environment-induced polarization. In methyl THF the distortion is not so big as in acetonitrile, and the red Stocks shift for emission (509 nm) is not so large, Fig. 2b. This emission in solid THF solvent at 77K can also be ascribed to fluorescence with 0-0 band at 509 nm and vibronic 0-1 satellite at 541 nm, Fig. 2b. The vibrational interval is equal to 1160 cm^{-1} corresponds to CCH bending frequency. But, an additional peak at 587 nm in solid THF glass is not a vibronic progression. This is a new $T_1 \rightarrow S_0$ emission, since vibrational interval could be too big (1418 cm^{-1}) in the case of the same CCH vibration progression.

In the glass with ethyl iodide admixture at 77K the additional emission peak at 587 nm is much more enhanced, Fig. 2b. This is explained by the well-known external heavy atom (EHA) effect because iodide in solvent provides enhancement of SOC in organic chromophores and increases, transition dipole moment of the $T_1 \rightarrow S_0$ transition [2,3]. The EHA can also increase the intersystem crossing $S_1 \rightarrow T_1$ rate and additionally enhance phosphorescence emission at Fig. 2b in the dashed curve. Thus, the emission in solid THF solvent at 77K can be ascribed to phosphorescence in both cases, with and without EHA effect, Fig. 2b. It consists of 0-0 band at 587 nm and vibronic 0-1 satellite at 638 nm. The new vibronic interval 1363 cm^{-1} in phosphorescence spectrum is higher than that in fluorescence (1161 cm^{-1}). This is quite natural since the $S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$ transitions have completely different origins for their radiative activity [3].

For the optimized S_0 and T_1 structures the $\Delta E_{(S_0-T_1)}$ energy gap is calculated to be 32.8 kcal/mol (1.43 eV). The UHF PM3 method is known to underestimate these $\Delta E_{(S_0-T_1)}$ values [6,7]. This comment is consistent with the observed fluorescence and phosphorescence spectra in Fig. 2b. The small $\Delta E_{(S_1-T_1)}$ energy gap of about 0.3 eV at the optimized S_1 and T_1 equilibrium geometries is in a good agreement with the measurements of Ref. [1]. The calculated radiative lifetime of fluorescence (with the observed wave length) is equal 5 ns in acetonitrile and 5.8 ns – in methyl THF. These estimations are in a reasonable agreement with experimental measurement: 6.9 ns in a neutral Hexane [1]. The delayed fluorescence lifetime (0.176 ms) definitely corresponds to TADF emission being 300000 times longer.

The studied fabricated OLED was composed of all typical layers and components ITO/PEDOT:PSS/NPD/1/BPhen/LiF/Al [1,2]. The hole blocking layer 4,7-Diphenyl-1,10-phenanthroline (BPhen) was placed after the emissive layer of compound **1** closer to the aluminium cathode in order to confine the excitons in the emissive layer. As a hole injecting layer was used poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS). A well-known N,N'-di-(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPD) as a hole transporting layer [2] was implemented. Indium-Tin-Oxide (ITO) catode and LiF as electron injector are used as usual traditional components [1,2]. The calculated properties of compound **1** correspond well to a high quality of fabricated OLED with efficient TADF emission [1].

3. Conclusions

Electronic structure of the ground and excited states of the N-methylacridone-di(2,2'-dinaphthylamine) molecule is studied by geometry optimization in the framework of semiempirical self-consistent field method. The molecule represents the A-D-A type compound, where acridone moiety is a donor (D) and naphthylamine is an acceptor (A) of electron density, according to classification of the authors of ref. [1], whose who synthesized this compound and used it for OLED fabrication. Our calculations show that the A–D–A type classification does not fully correspond to the electron density distribution and the molecule is not symmetric. This asymmetry strongly increased in the first excited triplet (T_1) and singlet (S_1) states. Thus, the vertical $S_0 \rightarrow S_1$ excitation is predicted with too high energy and 0–0 transition – with too low excitation energy. Strong distortion in excited states explains the Stocks shift and vibronic progression in the luminescence spectra and its temperature and solvent dependence.

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**КВАНТОВО-ХІМІЧНІ РОЗРАХУНКИ
ПОХІДНОГО АКРИДОН-2,2'-ДИНАФТИЛАМІНУ ЯК ЕМІТЕР ДЛЯ ОЛЕДІВ З
ТЕРМОАКТИВОВАНОЮ ЗАТРИМАНОЮ ФЛЮОРЕСЦЕНЦІЄЮ**

Анотація. Електронна структура нещодавно синтезованої молекули похідного N-метилакридону в основному та збудженому станах розраховується методом самоузгодженого поля РМЗ з оптимізацією геометрії. Розрахунки показують, що молекула несиметрична в основному стані, і для збудженого триплетного стану прогнозується сильне асиметричне спотворення. Це пояснює тривалий вібраційний прогрес у спектрах випромінювання та низьку зовнішню квантову ефективність виготовленого органічного світлодіода на основі цієї сполуки.

Ключові слова: термічно активована затримана флуоресценція, вібронне переміщення, акридони, архітектура та інтерфейс OLED, спин-орбітальна взаємодія, самоузгоджене поле.

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