Supplementary materials

Theoretical Study of Structure and Photophysics of Homologous Series of Bis(arylydene)cycloalkanones

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Table S1 Comparison of experimental and calculated chemical shifts

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Cyclobutanones | | | | | | | | | | | | | |
| **Proton**  **group** | | 4-H | | | | 4-OMe | | | | 3,4-OMe | | | |
| Calculation | | Experiment | | Calculation | | Experiment | | Calculation | | Experiment | |
| 4H (С(3)Н2) | | 3.93 | | 3.89 | | 3.80 | | 3.78 | | 3.77 | | 3.81 | |
| 2H (methine) | | 7.36 | | 7.19 | | 7.23 | | 7.11 | | 7.20 | | 7.10 | |
| Cyclopentanones | | | | | | | | | | | | | |
| **Proton**  **group** | | 4-H | | | | 4-OMe | | | | 3,4-OMe | | | |
| Calculation | | Experiment | | Calculation | | Experiment | | Calculation | | Experiment | |
| 4H (С(3-4)Н2) | | 3.25 | | 3.12 | | 3.06 | | 3.08 | | 3.05 | | 3.08 | |
| 2H (methine) | | 7.86 | | 7.6 | | 7.67 | | 7.56 | | 7.66 | | 7.51 | |
| Cyclopentanones | | | | | | | | | | | | | |
| **Proton**  **group** | | 4-H | | | | 4-OMe | | | | 3,4-OMe | | | |
| Calculation | | Experiment | | Calculation | | Experiment | | Calculation | | Experiment | |
| 4H (С(3,5)Н2) | | 3.05 | | 2.96 | | 3.00 | | 2.94 | | 3.11 | | 2.95 | |
| 4H (С(4)Н2) | | 1.69 | | 1.80 | | 1.70 | | 1.80 | | 1.75 | | 1.81 | |
| 2H (methine) | | 8.38 | | 7.72 | | 8.28 | | 7.67 | | 8.27 | | 7.66 | |

|  |  |
| --- | --- |
|  |  |

Figure S1 Calculated and experimental chemical shifts in 4-H (solid), 4-OMe (dashed), and 3,4-OMe (dotted).

|  |  |
| --- | --- |
| Cyclobutanone | |
|  |  |
| Cyclopentanone | |
|  |  |
| Cyclohexanone | |
|  |  |

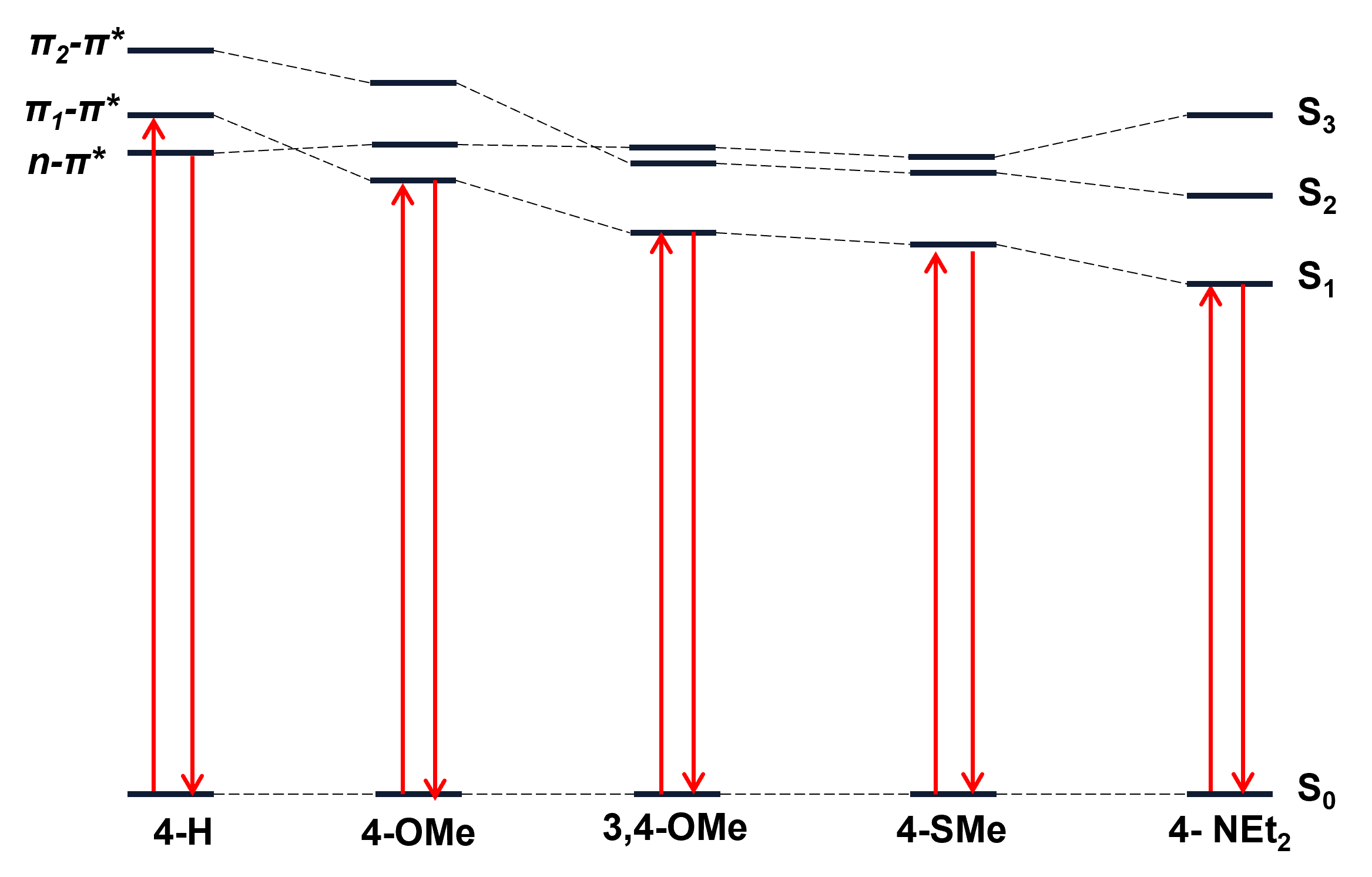
Figure S2 Correlations between the calculated HOMO and LUMO energies and experimental oxidation and reduction potentials.

|  |
| --- |
| Cyclobutanone |
|  |
| Cyclopentanone |
|  |
| Cyclohexanone |
|  |

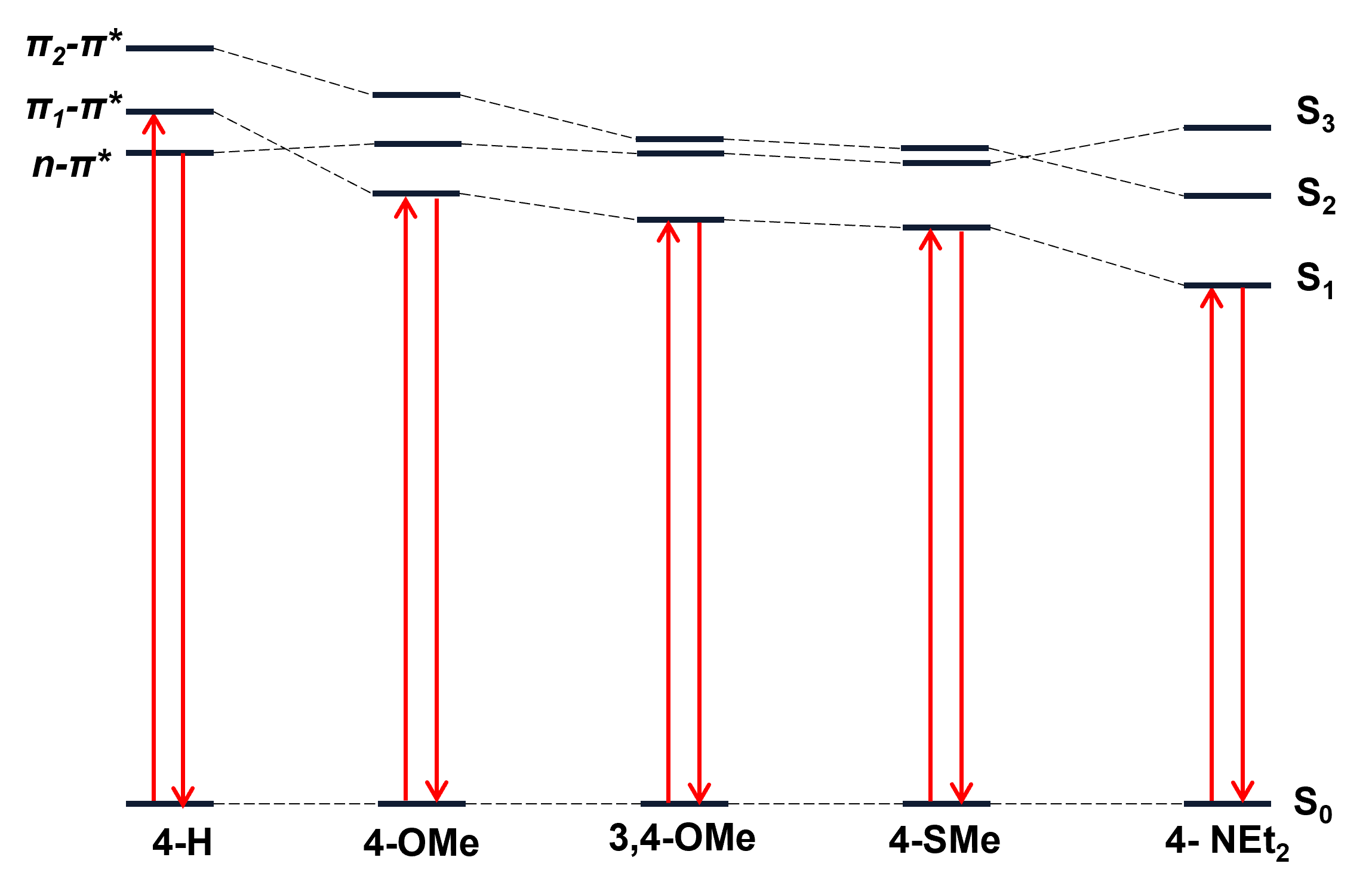
Figure S3. Correlations between the calculated HOMO-LUMO gap and experimental gap between the oxidation and reduction potentials.

|  |  |
| --- | --- |
|  |  |
| **a** | **b** |

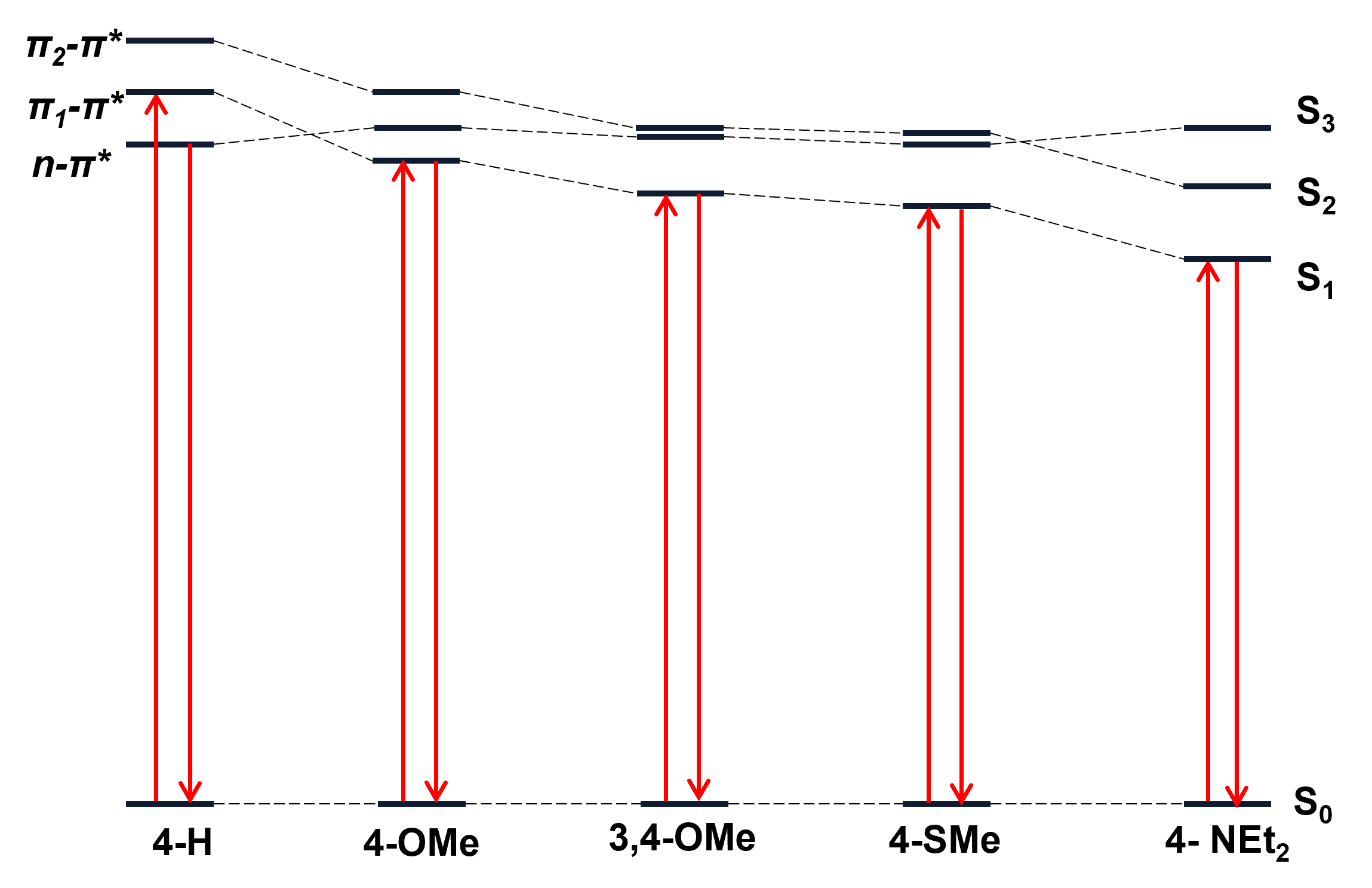
Figure S4. Oscillator strengths of the first and second ππ\* transitions.



**(a)**



**(b)**

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**(c)**

Figure S5. Energy diagrams of the excited states of (E,E) isomer in cyclobutanone (a), cyclopentanone (b) and cyclopentanone (c) series.

Table S2 Experimental and calculated electronic transitions

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Cyclobutanones | | | | | | | |
|  | | **λabs, nm** | | | **λfl, nm** | | |
| **Dienone** | | **Experiment** | **Calculation (Osc. Strength)** | **type** | **Experiment** | **Calculation (τrad, ns)** | **type** |
| **1a** | | 356 | 359 (0.90)  378 (2·10-7) | π–π\*  n–π\* | - | 411 (2.3·107) | n–π\* |
| **1b** | | 385 | 393 (1.10) | π–π\* | - | 419 (2.28) | π–π\* |
| **1c** | | 401 | 427 (0.83) | π–π\* | 505 | 446 (3.48) | π–π\* |
| **1d** | | 402 | 432 (1.11) | π–π\* | 522 | 452 (2.62) | π–π\* |
| **1e** | | 481 | 471 (1.23) | π–π\* | 575 | 491 (2.86) | π–π\* |
| Cyclopentanones | | | | | | | |
|  | | **λabs, nm** | | | **λfl, nm** | | |
| **Dienone** | | **Experiment** | **Calculation (Osc. Strength)** | **type** | **Experiment** | **Calculation (τrad, ns)** | **type** |
| **2a** | | 347 | 371 (1.16)  379 (6.5·10-5) | π–π\*  n–π\* | - | 401 (1.0·107) | n–π\* |
| **2b** | | 380 | 395 (1.36) | π–π\* | - | 422 (1.8) | π–π\* |
| **2c** | | 395 | 420 (1.22) | π–π\* | 500 | 439 (2.2) | π–π\* |
| **2d** | | 396 | 424 (1.42) | π–π\* | 508 | 458 (2.0) | π–π\* |
| **2e** | | 471 | 472 (1.79) | π–π\* | 562 | 482 (1.9) | π–π\* |
| Cyclohexanones | | | | | | | |
|  | | **λabs, nm** | | | **λfl, nm** | | |
| **Dienone** | **Experiment** | | **Calculation (Osc. Strength)** | **type** | **Experiment** | **Calculation (τrad, ns)** | **type** |
| **3a** | 326 | | 348 (0.92)  375 (0.07) | π–π\*  n–π\* | - | 414 (778) | n–π\* |
| **3b** | 356 | | 385 (1.02) | π–π\* | - | 431 (2.90) | π–π\* |
| **3c** | 370 | | 404 (1.04) | π–π\* | - | 432 (2.26) | π–π\* |
| **3d** | 368 | | 410 (1.21) | π–π\* | - | 441 (2.02) | π–π\* |
| **3e** | 445 | | 455 (1.54) | π–π\* | 562 | 495 (2.46) | π–π\* |