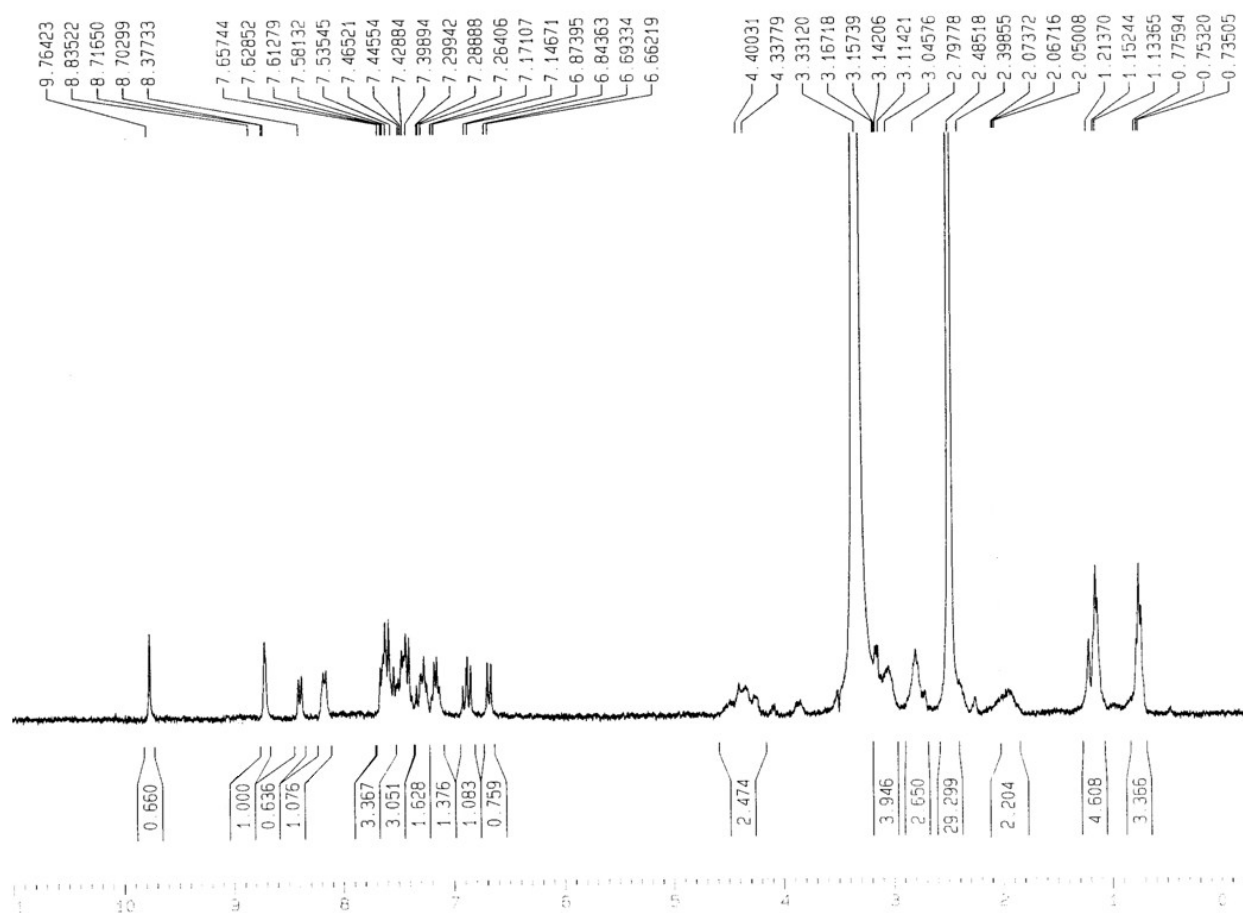
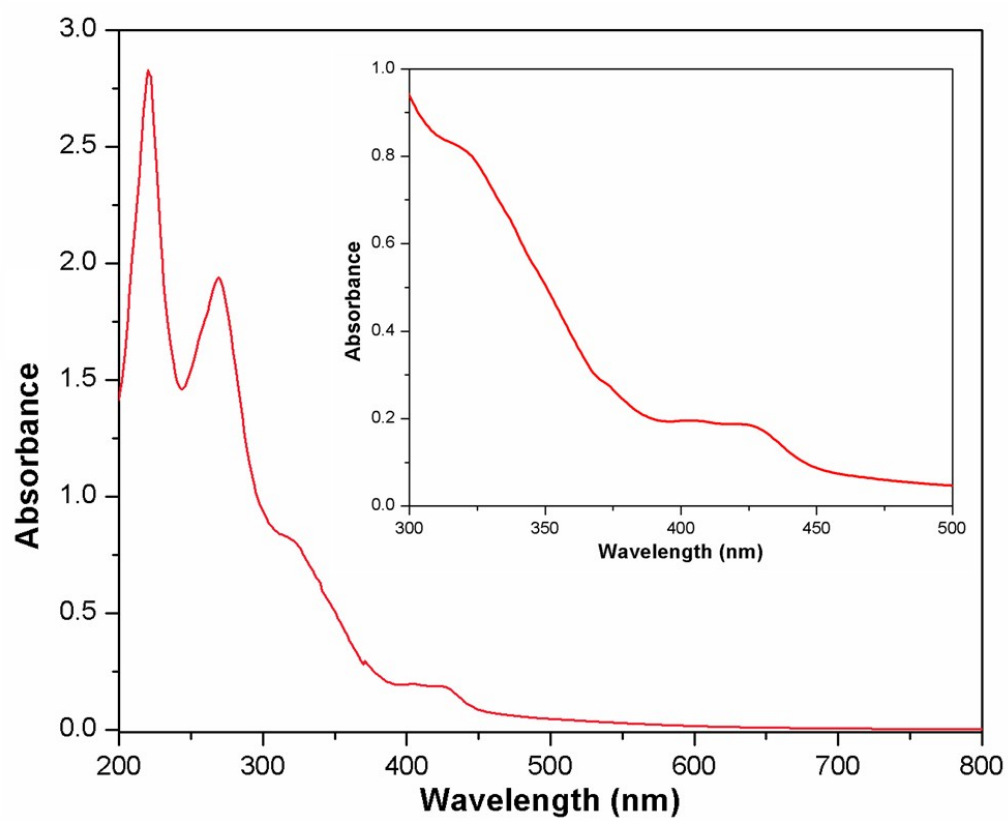
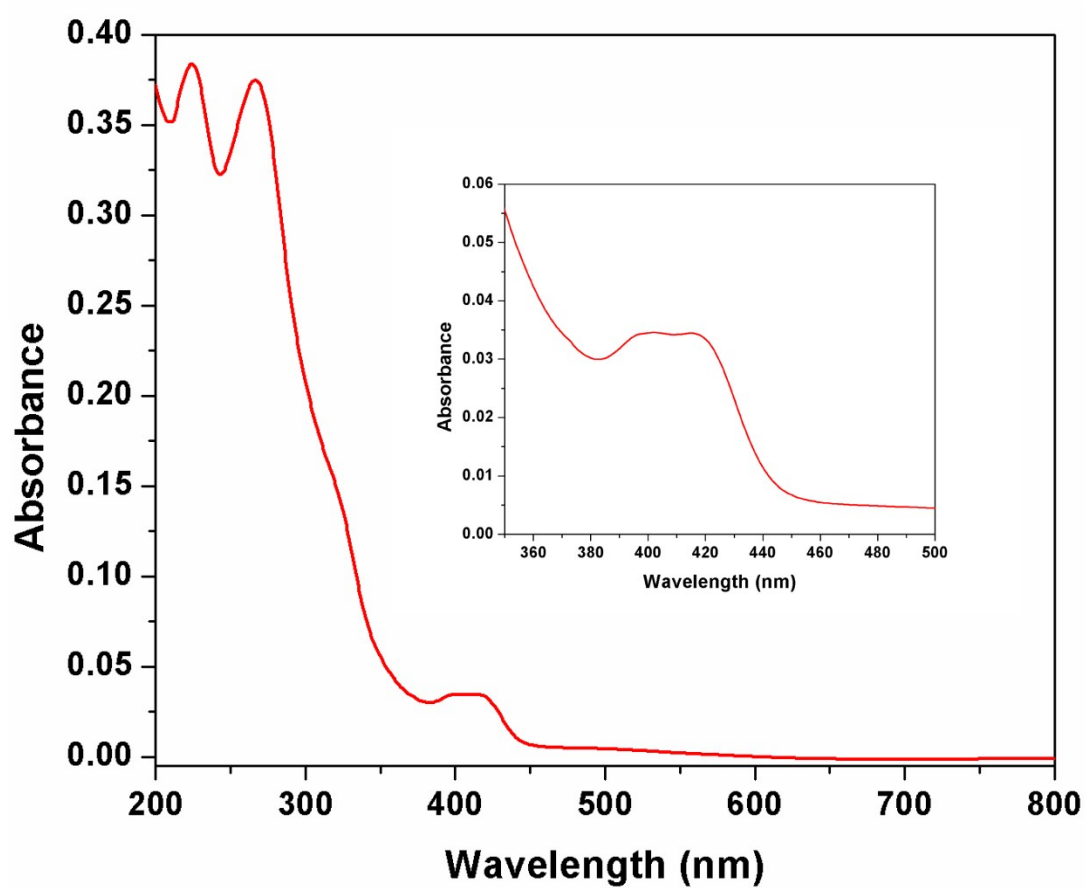




**Figure S1:**  $^1\text{H}$  NMR spectrum of complex 1.



**Figure S2:**Electronic spectrum of complex **1** with highlighted LMCT band (in inset).



**Figure S3:**Electronic spectrum of complex 2 with highlighted LMCT band (in inset).

**Table S1:** Geometric features (distances in Å and angles in °) of C–H··· $\pi$  interactions obtained for the complexes **1** and **2**.

| Complex  | C–H···Cg(Ring)       | H···Cg (Å) | C–H···Cg (°) | C···Cg (Å) |
|----------|----------------------|------------|--------------|------------|
| <b>1</b> | C(16)–H(16)···Cg(4)  | 2.70       | 169          | 3.634      |
|          | C(27)–H(27B)···Cg(4) | 2.60       | 161          | 3.556      |
| <b>2</b> | C(20)–H(20)···Cg(4)  | 3.243      | 115          | 3.740      |
|          | C(22)–H(22A)···C(6)  | 2.989      | 152          | 3.883      |
|          | C(13)–H(13A)···C(4)  | 2.823      | 171          | 3.803      |
|          | C(15)–H(15A)···C(4)  | 3.364      | 125          | 4.004      |

Cg(4) = Centre of gravity of the ring **R**<sup>4</sup> [C(1)–C(2)–C(3)–C(4)–C(5)–C(10)] for **1** and **2**.

**Table S2:** Geometric features (distances in Å and angles in °) of other noncovalent interactions for complex **1**.

| D–H···A            | D–H (Å) | H···A (Å) | D–H···A (°) | D···A (Å) |
|--------------------|---------|-----------|-------------|-----------|
| C(11)–H(11)···O(3) | 0.95    | 2.51      | 119         | 3.080(4)  |
| C(11)–H(11)···N(3) | 0.95    | 2.83      | 162         | 3.744(3)  |
| C(4)–H(4)···N(3)   | 0.95    | 2.71      | 133         | 3.426(4)  |
| C(3)–H(3)···N(5)   | 0.95    | 2.99      | 130         | 3.670(5)  |

D = Donor, A = Acceptor

**Table S3: Cartesian coordinates of the optimized complex (H positions) 1**

| Complex 1 |            |            |            |   |            |            |            |
|-----------|------------|------------|------------|---|------------|------------|------------|
| Co        | -0.9848920 | 0.4464614  | -0.4971383 | C | 1.5051073  | 0.0514615  | 6.5798597  |
| O         | -1.5748919 | 1.2854612  | 1.1128612  | H | 1.8940900  | 0.0144084  | 7.5990400  |
| O         | 0.5671075  | 1.5274611  | -0.3861384 | C | 5.0901063  | 1.8024610  | -3.6051374 |
| N         | -0.4238922 | -0.4015383 | -2.0821379 | H | 5.7926679  | 2.6119375  | -3.3959236 |
| N         | -2.7278915 | -0.6495383 | -0.6871383 | C | 1.0971074  | -1.9285379 | 2.1758609  |
| N         | -1.4338919 | 2.3384609  | -2.4501378 | H | 1.3245258  | -2.7216438 | 1.4634670  |
| N         | -1.8698918 | 1.8864610  | -1.4321381 | C | -5.2728908 | -0.5615383 | -0.5211383 |
| C         | 0.7141075  | -0.2665384 | -2.6571377 | H | -5.4527647 | -0.7907531 | -1.5807673 |
| H         | 0.8927440  | -0.8692450 | -3.5603274 | H | -6.0847483 | 0.1056048  | -0.1974217 |
| C         | 0.3041076  | -0.8425382 | 1.6948611  | H | -5.3729837 | -1.4942478 | 0.0492999  |
| C         | 1.7541072  | 0.6464614  | -2.2991378 | C | 1.2491073  | -0.9145382 | 4.3818603  |
| C         | -0.0468923 | 0.1974615  | 2.5918608  | C | 3.2921068  | -0.2545384 | -4.1001373 |
| C         | 2.9571069  | 0.6974613  | -3.0901376 | H | 2.6304910  | -1.0943370 | -4.3078700 |
| N         | -1.0828920 | 2.8454607  | -3.4241375 | C | -3.9408912 | 0.1374615  | -0.2961384 |
| C         | 0.4781076  | 0.1814615  | 3.9648604  | H | -3.8847557 | 1.0756950  | -0.8594484 |
| C         | 3.9081066  | 1.7294611  | 2.8511377  | H | -3.8123768 | 0.4132885  | 0.7569892  |
| C         | -1.0358920 | 1.1334612  | 2.2468609  | C | 0.7601075  | 1.1594612  | 6.1668598  |
| H         | -1.4120554 | 1.8017508  | 3.0400577  | H | 0.5850658  | 1.9843093  | 6.8591751  |
| C         | 1.7481072  | 0.9715382  | -5.7148599 | C | 2.5351070  | 2.5834608  | -1.0321382 |
| H         | 2.3404778  | -1.8377243 | 6.0159279  | H | 2.3405679  | 3.2921281  | -0.2276179 |
| C         | 5.3671062  | 0.8714613  | -4.5801372 | C | 4.4641064  | -0.1555384 | -4.8141371 |
| H         | 6.2908863  | 0.9347129  | -5.1566198 | H | 4.6849598  | -0.9070250 | -5.5748399 |
| C         | -2.7658915 | -0.9145382 | -2.1601379 | C | 1.5361073  | -1.9705379 | 3.4658606  |
| H         | -3.0300033 | 0.0270801  | -2.6573328 | H | 2.1308930  | -2.8162704 | 3.8185737  |
| H         | -3.5282679 | -1.6698154 | -2.4132573 | O | -0.0808923 | -0.9345382 | 0.4628614  |
| C         | 1.5701073  | 1.5484611  | -1.2241381 | C | -2.7058915 | -1.9745379 | 0.0038615  |
| C         | 3.6361067  | 2.6704608  | -1.8191380 | H | -1.7184887 | -2.4141349 | -0.1751907 |
| H         | 4.3588257  | 3.4743225  | -1.6554098 | H | -3.4553776 | -2.6387197 | -0.4654929 |
| C         | 0.2511076  | 1.2324612  | 4.8768602  | C | -2.9428915 | -1.9335379 | 1.5108611  |
| H         | -0.2928376 | 2.1260817  | 4.5787056  | H | -3.9736462 | -1.6644576 | 1.7730149  |
| C         | -1.4058919 | -1.3675381 | -2.6071377 | H | -2.2675670 | -1.2261252 | 2.0036992  |
| H         | -1.1648665 | -2.3643219 | -2.2041708 | H | -2.7410566 | -2.9299280 | 1.9271039  |
| H         | -1.3607792 | -1.4361549 | -3.7075526 |   |            |            |            |

**Table S4: Cartesian coordinates of the optimized complex (H positions) 2**

| Complex 2 |            |            |            |   |            |            |            |
|-----------|------------|------------|------------|---|------------|------------|------------|
| Co        | -0.7709659 | 0.4278643  | 0.0022203  | C | -2.6209654 | -1.6551351 | -0.2177796 |
| O         | 0.7320337  | 1.2908640  | -0.7097795 | H | -3.0101171 | -1.2150063 | -1.1444362 |
| O         | 0.3140338  | -0.0321356 | 1.5212199  | H | -3.3451166 | -2.3982899 | 0.1551930  |
| O         | -1.2569657 | 2.1418638  | 0.7052201  | C | -3.6559651 | 0.3278643  | 0.7312201  |
| N         | -0.3219660 | -1.2371352 | -0.7647794 | H | -3.7021341 | 0.7569517  | -0.2771413 |
| N         | -2.4369654 | -0.5341354 | 0.7552201  | H | -3.4634823 | 1.1714663  | 1.4038151  |
| N         | -1.8259656 | 0.9268641  | -1.5587792 | C | -4.9639647 | -0.3731355 | 1.0802200  |
| N         | -1.3039657 | 0.9478641  | -2.6367789 | H | -5.2264712 | -1.1560477 | 0.3562751  |
| N         | -0.8689659 | 0.9938641  | -3.7087786 | H | -5.7788957 | 0.3647849  | 1.0637397  |
| C         | 3.0700330  | -2.3871349 | -3.0137788 | H | -4.9558173 | -0.8236079 | 2.0825772  |
| H         | 2.2648344  | -3.1082186 | -2.8853801 | C | -2.2429655 | -1.1201353 | 2.1222197  |
| C         | 4.1980327  | -2.7861348 | -3.6897786 | H | -1.2588605 | -1.6025548 | 2.1185946  |
| H         | 4.2589634  | -3.8070222 | -4.0715730 | H | -2.9949516 | -1.9158897 | 2.2795010  |
| C         | 5.2640324  | -1.9101351 | -3.8877786 | C | -2.2979655 | -0.1351356 | 3.2572194  |
| H         | 6.1568638  | -2.2504503 | -4.4149660 | H | -1.6744353 | 0.7457271  | 3.0649846  |
| C         | 5.1760324  | -0.6331354 | -3.4337787 | H | -1.9211230 | -0.6165164 | 4.1704948  |
| H         | 5.9915083  | 0.0759225  | -3.5930399 | H | -3.3183295 | 0.2122612  | 3.4694630  |
| C         | 4.0180328  | -0.1801355 | -2.7577789 | C | -0.5579659 | 2.7568636  | 1.5702199  |
| C         | 3.9130328  | 1.1668641  | -2.3107790 | C | -0.8699659 | 4.2148632  | 1.7212199  |
| H         | 4.7428086  | 1.8478731  | -2.5166389 | H | -0.6127680 | 4.7289267  | 0.7827348  |
| C         | 2.8120331  | 1.6068640  | -1.6647792 | H | -0.3274534 | 4.6913503  | 2.5471138  |
| H         | 2.7127360  | 2.6399039  | -1.3305497 | H | -1.9509679 | 4.3489849  | 1.8697985  |
| C         | 1.7200334  | 0.7388642  | -1.3617793 | C | 0.4360338  | 2.1838638  | 2.3592197  |
| C         | 1.7910334  | -0.6041354 | -1.7727792 | H | 0.9289930  | 2.8146575  | 3.0963453  |
| C         | 2.9490331  | -1.0671353 | -2.5077790 | C | 0.7640337  | 0.8318642  | 2.3422197  |
| C         | 0.7330337  | -1.5091352 | -1.4447793 | C | 1.6890334  | 0.3068643  | 3.3972194  |
| H         | 0.8432665  | -2.5428020 | -1.8042982 | H | 1.1117703  | -0.3175413 | 4.0975721  |
| C         | -1.2899657 | -2.3041349 | -0.4807795 | H | 2.1835030  | 1.1021998  | 3.9676533  |
| H         | -0.9424673 | -2.8625676 | 0.4045585  | H | 2.4492866  | -0.3428965 | 2.9405669  |
| H         | -1.3664821 | -3.0237725 | -1.3140182 |   |            |            |            |